Controls On Stream Dissolved Organic Carbon Concentration In Several Small Catchments In Southern Quebec

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Concentration In Streams

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PREFACE

I would like to thank Professor T.R. Moore for providing guidance and counselling throughout my thesis work. I would also like to thank Professor J. Rasmussen for his comments and guidance. Special thanks goes to Ms. P. Kestelman, Department of Geography, Technician for helping me with obtaining equipment and supplying some good humour at times. I would also like to thank my colleague and friend Mike Dalva for sharing some his data with me.

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CONTROLS ON STREAM DISSOLVED ORGANIC CARBON CONCENTRATION IN SEVERAL SMALL CATCHMENTS IN SOUTHERN QUEBEC

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Abstract- Dissolved organic carbon (DOC) concentration in stream water was predicted from catchments (0.6-37 km^2) using simple and multiple regression based on physical characteristics of the catchments. Physical characteristics such as drainage class, percentage wetland, and slope were easily obtainable from maps, aerial photographs, and publications. Prediction of DOC concentration was carried out in two phases. The first phase involved 8 catchments and a simple regression of ln(DOC) against ln(drainage) had an r^2 of 0.89. The catchments ranged in size from 3 to 9 km^2 and were divided into four wetland and four non-wetland catchments. The second phase involved 42 catchments ranging in size from 0.6 to 37 km^2 This phase of the study was further broken down by sample date and region and a multiple regression was used The ln(DOC concentration) was predicted using drainage class, percentage wetland, and slope and the r^2 values ranged from 0 32 up to 0 73

Seasonal variations in DOC concentration were determined using the residuals of a regression of ln(DOC) against Julian date, plotted against the Julian date. Seasonality was shown by a sine-wave pattern (Grieve, 1982). Only three non-wetland catchments (in the first phase) exhibited this sine-wave pattern Patterns in the other 5 catchments could not be ascribed to season alone. Seasonal variations in the 42 catchment group were shown by the changing predictive ability of the model over a four month period Seasonal variations in electrical conductivity (Ec), pH, cations, and anions were also observed

Discharge was found to be positively related to DOC concentration for non-wetland catchments, but the relationship was not significant for wetland catchments. Differences in DOC sources, sinks, storage areas, and pathways between the two types (wetland and non-wetland) of catchments were responsible for the different discharge relationships Changing season also caused changes in the sources, sinks, storage areas, and pathways which caused different DOC concentrations in streams over the study period.

EVALUATION DE LA CONCENTRATION DE CARBONE ORGANIQUE DISSOUS DANS LES COURS D'EAU DE PLUSIEURS PETITS BASSINS HYDROGRAPHIQUES DU SUD DU QUEBEC

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Résumé - La concentration de carbone organique dissous (COD) dans les eaux de drainage a pu être déterminée par une analyse statistique (régressions simple et multiple) des caractéristiques physiques de petits bassins hydrographiques (entre 0.6 et 37 km^2 de superficie). L'étude de cartes, photographies aériennes et autres documents a permis de déterminer des caractéristiques comme le drainage, le pourcentage de terres mal drainees ainsi que la pente. Dans un premier temps, une régression multiple [ln(COD) en abscisse et ln(drainage) en ordonnée] effectuée pour 8 bassins hydrographiques ayant entre 3 et 9 km^2 de superficie a révélé une valeur de r^2 de 0,89. Quatre de ces bassins avaient des conditions de drainage médiocres. Dans un deuxième temps, 42 bassins versants ayant entre 0.6 et 37 km^2 de superficie et ayant prealablement éte subdivises par région et date d'échantillonnage ont été analyses par la méthode de régression multiple Les données relatives au drainage, a la pente ainsi que le pourcentage des terres mal drainees ont permis d'evaluer ln(concentration de COD) les valeurs de r^2 variaient entre 0,32 et 0,73

Un graphique mettant en cause le résidu d'une régression de ln(COD) en fonction de ln(jour julien) en abscisse et le jour julien en ordonnee a permis de determiner les variations saisonnières (observables sous la forme d'oscillations sinusoidales) de la concentration de COD. Toutefois, on a observe de telles oscillations que dans le cas de trois bassins bien draines (sur les huit premiers analyses) Il a été impossible d'associer le pattern observable sur l'image graphique des 5 autres bassins uniquement aux variations saisonnières Les variations saisonnieres dans le cas des 42 bassins hydrographiques se sont traduites par une variation des performances du modele sur une periode de 4 mois Des variations saisonnieres des valeurs de conductivité electrique, du pH ainsi que du nombre de cations et d'anions ont par ailleurs ete observees.

On a pu etablir une relation croissante entre la quantité d'eau provenant des bassins bien drainés et la concentration de COD. Une telle relation n'a pu être determinee pour les zones mal drainees. Les differences obtenues d'un bassin a un autre dans les relations COD en fonction de la quantite d'ecoulement s'expliquent par la diversité de sources, puits, zones de transit et type d'ecoulement des eaux de ruissellement, selon les caracteristiques physiques des bassins. Par ailleurs, l'effet du changement des saisons sur les sources, puits, zones de transit et type d'ecoulement s'est traduit par des variations de concentration de COD dans l'eau.

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CHAPTER 1

INTRODUCTION

Dissolved organic carbon (DOC) in stream water is important for several reasons: a) as DOC concentration increases the pH of water generally decreases; b) DOC-rich waters are generally dark-coloured and light penetration is reduced, thereby affecting biological activity in streams and lakes; c) DOC has the ability to complex metals from soil and transport them into streams, causing higher than normal concentrations of metals in solution and sediments; d) unpleasant tastes can occur in DOC-rich water; and e) chlorination of DOC-rich water can produce carcinogenic compounds (Jackson, 1975; Caine, 1982; Thurman, 1985).

DOC found in stream water is a combination of fulvic and humic acids and other organic carbon compounds in dissolved form (Weber and Wilson, 1975). Humic acid may be a by-product of decomposition of the original lignin structure of plants, but Geissman and Crout (1969) point out the difficulty of characterising humic acids lies in the fact that no two humic acid by-products of lignin decomposition are alike. Wallis et al. (1981), McDowell and Wood (1984) and Thurman (1985) have shown that humic and fulvic acid concentrations in groundwater are functions of soil depth and soil adsorption characteristics. Shallow soils tend to supply both humic and fulvic acid while deeper soils supply less (or zero) fulvic acid.

In general, humic substances found in streams are of allochthonous origin from soil and plant material. In stream water, fulvic acid generally comprises 85% of the humic substances while humic acid makes up 15% (Thurman, 1985). The major functional groups of fulvic and humic acids are carboxyl, hydroxyl, carbonyl, lesser amounts of phenolic hydroxyl, and traces of carbohydrates and amino acids. DOC concentrations in streams range from 0.5 mg/l to 10 mg/l in clear water and from 10 to 50 mg/l in darker tea-coloured waters (Thurman, 1985).

Wetland waters have higher concentrations of fulvic and humic acids than lakes and rivers. The fulvic and humic acids make up 70 - 90% of all DOC in wetland water (Thurman, 1985). The humic substances supplied by emergent plants is the main reason for the higher fulvic and humic acid percentages. Humic substances commonly buffer pH of water and transport trace metals, such as iron, aluminum, copper, cadmium and chromium (Sholkovitz and Copland, 1981; Tipping, 1981; Thurman, 1985). DOC concentrations of wetland water range from 10 to 30 mg/l and can be higher (Thurman, 1985). The higher DOC concentration may be due to slow decomposition of plant matter, which is in turn due to waterlogging of soils, lack of oxygen, and low pH (3-4). The low pH causes fungi to be one of the major organisms of organic decomposition. Under anaerobic conditions fungal activity ceases and humic substances can accumulate in the water (Thurman, 1985).

SOURCES, SINKS, AND STORAGE AREAS OF DOC IN CATCHMENTS

Sources and Sinks of DOC

Stream DOC can be derived from either terrestrial or aquatic sources. Source areas of DOC in a catchment are plant material (live and decomposing), animal (living and decaying tissue), animal and microbial respiration, and any other organic substances (e.g. peaty soils, organic soil horizons) that produce humic and fulvic acids or organic carbon compounds that subsequently dissolve in water. Of importance to this study is the determination of whether catchments with a significant wetland area produce higher DOC concentrations in stream water than non-wetland catchments.

Table 1 lists the sources and storage areas of DOC which can act separately or in conjunction with precipitation to supply DOC to streams. As indicated by Table 2, precipitation supplies little DOC (1 - 3 mg/l) as a source, but as a transport mechanism (i.e. throughfall and stemflow) it can leach organic matter from vegetation. Precipitation, therefore, can help release DOC from other sources and storage areas, such as vegetation, wetlands, and organic soil horizons.

DOC compounds can be leached off vegetation surfaces and reach the ground surface either by falling directly (leaf drip) or by flowing along stems and trunks. Both sources can supply DOC either directly to a stream or indirectly by falling on the ground surface and then moving toward a stream. Throughfall and stemflow concentrations range from less than 10 up to 356 mg/l (Table 2). The input of DOC from vegetation changes throughout the year and reaches a peak during the growing season and summer (Meyer and Tate, 1983; McDowell and Wood, 1984). Newly shed leaves falling into the stream can release DOC during the growing season and autumn (Mulholland, 1981; Meyer and Tate, 1983; Tate and Meyer, 1983).

Ground sources of DOC include leaf litter and other plant material, soil organic horizons, and organic matter in the soil. Leaf litter can release DOC into either overland flow or into the underlying

TABLE 1

Sources and Storage Areas of DOC Within a Catchment

SOURCES
Precipitation
Terrestrial Vegetation (living)
Aquatic Vegetation (living)
Soil Organic Matter
Stream Channel Sediments
Suspended Sediments
Peat
Decaying Plant Material
Leaf Litter And Branches
STORAGE AREAS
Soil Horizons
Dry Stream Channel Sediments
Channel Pools
Organic Matter (terrestrial)
Organic Matter (aquatic)
Stream Sediments
Leaf Litter
Soil Around Tree Bases

soil through infiltration. Leaf litter and twigs can also be blown into streams by winds, creating another source of DOC (Meyer and Tate, 1983; McDowell and Wood, 1984). DOC released into overland flow can reach streams quickly and cause an increase in DOC concentration in the stream. Because saturation of leaf litter is dependent on precipitation, this source of DOC is generally only available during storm events and when leaves are present on the ground. In the absence of overland flow, DOC leached from the saturated leaves will infiltrate the underlying soil or flow through organic horizons and it may take several years before the DOC reaches a stream (Wallis et al., 1981; Meyer and Tate, 1983) or the DOC may be partially adsorbed by soil horizons that contain iron and aluminum oxides (McDowell and Wood, 1984; Thurman, 1985).

TABLE 2

Observed DOC Concentrations From Different Sources and Pathways in a Catchment (all values in mg/l)

Study	ppt	thfl	stem	seep	sow	soh
Dalva (in press)	1 - 3	8 - 16	18 - 105	-	-	-
Foster & Grieve (1982)	-	25 *	-	-	-	-
Meyer & Tate (1983)	1	-	-	0.3-0.7	-	-
Moore (1989)	1	16	356	-	12	56
Moore & Jackson (1989)	1	21	47	-	46	46
Mulholland (1981)	-	18	29	-	-	-
Wallis et al. (1981)	3	8	-	-	6 - 21	-

-Note: ppt=precipitation; thfl=throughfall; stem=stemflow; seep=seepage from groundwater and springs; sow=soil water; soh=soil organic horizon. *-value is an average of 8 samples.

Soil organic horizons and peat soils supply DOC to local streams either through groundwater (in well drained soils) or overland flow and shallow subsurface flow (in bogs and other wetlands). In shallow soils, where the absence of horizons with high concentrations of iron and aluminum oxides limits DOC adsorption, subsurface flow moves DOC compounds through the soil into local streams faster than groundwater flow through deeper soils. The significance of the amount of DOC supplied from organic horizons is dependent on soil depth, precipitation input, and antecedent wetness conditions (Wallis et al., 1981; Taylor and Pearce, 1982; Meyer and Tate, 1983).

In-stream sources of DOC are not directly related to the input of precipitation and are relatively constant suppliers (dependent on temperature and season) (Mulholland, 1981; Meyer and Tate, 1983). Channel sediments, benthic organisms and in-stream plant material (living and dead) supply organic materials to the stream that can form DOC compounds. In-stream sources may not fluctuate with changing discharge during storms (unless velocity of storm flow rises above a threshold level), as do terrestrial sources, but in the absence of input from terrestrial sources these in-stream sources can be depleted (Wetzel and Manny, 1977; Meyer and Tate, 1983). Channel sediments can collect in still water and pools in the stream bed where velocities are reduced. Areas in the stream bed where organic-laden material accumulates are termed retention devices (Naiman, 1982). Naiman (1982) and Clair and Freedman (1986) include waterfalls and ponds formed behind beaver or debris dams in the definition of retention devices. Mulholland (1981) showed how muck on the bottom of swamps can be a source of DOC during hot weather when the material warms and rises from the bottom toward the surface liberating stored DOC.

Benthic organisms, such as insects, invertebrates, bacteria, algae, and microbes can break down vegetation particles that fall into or grow in streams. Respiration of aquatic organisms, of all sizes, produces CO_2 which can be used in the formation of organic carbon compounds in the stream water (Mulholland, 1981). Terrestrial organisms (e.g. leaf shredders) can supply plant material to streams which decompose and produce DOC (Meyer and Tate, 1983). Aquatic plants are also sources of DOC. Decomposition of woody fibres in stream water can release DOC into the stream through lignin break down processes (Geissman and Crout, 1969) Rates of DOC production from biologic sources are dependent on stream water temperature and production increases during the growing season (Meyer and Tate, 1983).

Storage Areas of DOC

Table 1 lists areas where DOC can remain stored until released by a precipitation event. Several storage areas are the same as sources, with one difference. Storage areas are not true sources because they do not produce new DOC compounds, but supply stored DOC to the hydrologic system under certain conditions. During storm events and flood flows the storage areas become sources of DOC but they are secondary not primary sources. As discharge increases, the submerged area of the channel widens causing any stored DOC in the formerly dry stream bed to be released and added to the flood flow DOC concentration (Meyer and Tate, 1983). Any dried soil that had DOC-rich water in it at saturation will be able to supply DOC to the stream during a flood flow that causes the soil to once again become saturated.

Terrestrial storage areas include the bases of trees (where stemflow collects), leaf litter, twigs and larger stem parts that have fallen to the ground, organic matter in soil and dry stream channels (saturated or filled during flood flow), and soil horizons that adsorb DOC. These storage areas are all precipitation-dependent and can only supply DOC during storm events when they are saturated or wetted.

In-stream storage areas are similar to their terrestrial counterparts in that they store DOC produced elsewhere and release it only under certain conditions. During baseflow conditions when stream velocity is reduced (relative to storm flow) DOC-rich sediments and free floating DOC compounds can accumulate in still water and pools in the stream channel. Retention devices can be classified as storage areas of DOC as well as sources (Naiman, 1982). Storage areas become sources as the discharge increases and velocity rises sufficiently to flush out the still and pooled parts of the channel.

Foster and Grieve (1982) and Meyer and Tate (1983) discussed the influence of successive storm events on the storage areas in catchments. There appears to be a flushing effect caused by the successive wetting of storage areas over a period of time. Storage areas can become depleted of DOC if they dry out between flood events. The time frame for flushing effects can be short (several weeks) or long (decades) according to Meyer and Tate (1983) and only long term data collection can establish a pattern.

TRANSPORT OF DOC TO STREAMS

Table 3 indicates the various pathways taken by water to reach a stream. In the previous section, several of these pathways, associated with precipitation (i.e stemflow, throughfall, and leaf drip), are discussed in conjunction with the sources and storage areas. Quickflow is of importance to the transport of DOC within a catchment. Wind is an important factor in carrying dust particles into a catchment and moving leaf litter, sticks and sediment into streams. Precipitation not only generates stemflow, throughfall and leaf drip, it is instrumental in increasing the rate of flow of groundwater (Lewis and Grant, 1979; Sklash and Farvolden, 1979; Wallis et al., 1981; Anderson and Burt, 1982; Taylor and Pearce, 1982; Tate and Meyer, 1983).

Meyer and Tate (1983) proposed four potential sources within a catchment for increased DOC concentration during storms. The four sources are: a) surface flow carries stored terrestrial DOC into streams; b) direct throughfall adds DOC to streams bypassing the soil matrix; c) particulate organic matter from previously dry streambeds can supply leached DOC to the stream; and d) DOC also can come from storage in the streambed and intermittent channels that are disturbed by flood flows (Meyer and Tate, p 39, 1983). As the amount of water available for transporting DOC within the catchment increases, so do the number of potential sites for DOC supply. The stream DOC concentration increases and more DOC is transported through the catchment. Streamflow is no longer the only means of DOC transport in the catchment as overland flow (where conditions warrant), subsurface flow, throughfall, stemflow, and return flow all add to the movement of DOC.

TABLE 3

Pathways of DOC to Streams

Pathway	Direct	Indirect
Precipitation	x	x
Stemflow	x	x
Throughfall	x	x
Overland Flow	x	
Subsurface Flow	x	x
Quickflow	x	
Root Channels		x
Animal Burrows	x	x

-Note: **Direct** means leading or falling directly onto the stream surface; **Indirect** means falling onto the ground and infiltrating into the soil before reaching the stream.

Storm events are very important in the overall transport of DOC from a catchment, not only do they cause increased movement of DOC during precipitation events, they also supply the soil moisture and groundwater that account for the movement of DOC between storm events. Table 4 summarizes previous studies on stormflow and DOC concentration.

Table 4

Effect of Stormflow on DOC Concentration in Stream Water

Study	Site	[DOC]	Hydrograph
Anderson & Burt (1982)	England	inc	F
Foster & Grieve (1982)	England	inc	-
Grieve (1984)	Scotland	inc *	F
Lewis & Grant (1979)	Colorado	inc	-
Meyer & Tate (1983)	North Carolina	inc	B
Moore (1989)	New Zealand	inc	R
Moore & Jackson (1989)	New Zealand	inc **	F
Mulholland (1981)	North Carolina	inc *	-
Naiman (1982)	Quebec	minimal	-

Note: inc=increase of DOC with increase in discharge; dec=decrease of DOC with increase in discharge; F=DOC concentration higher on falling limb of hydrograph; R=DOC concentration higher on the rising limb of hydrograph; B=both rising and falling limbs, of different storms, show increases; -=no stated relationship; *=wetland catchments; **=both wetland and non-wetland catchments.

Quickflow response to storm events is a function of topography and antecedent wetness conditions (Taylor and Pearce, 1982) and can cause a rise in DOC concentration in a stream. Throughflow is another term used to describe the movement of water through the soil system of a catchment (Burt, 1979; Anderson and Burt, 1982). In Southern Quebec, Dunne et al. (1975) identified saturation overland flow to be the dominant quickflow response on shallow, less permeable soil of gentle slope. Other areas in Southern Quebec with steeper slope exhibit rapid subsurface flow instead of overland flow (Dunne et al., 1975). In arid regions and areas of degraded agricultural land, Hortonian overland flow can be observed during intense rainfall events (Taylor and Pearce, 1982; Ward, 1984).

Wallis et al. (1981), Taylor and Pearce (1982), and Pearce et al. (1986) identified macro-pore flow as a component of subsurface flow. Macro-pores are created by animal burrows and root channels that no longer have living roots in them. Under certain conditions of rainfall intensity and saturation, the amount of flow through macro pores can be significant (Sklash and Farvolden, 1979; Wallis et al., 1981; Taylor and Pearce, 1982). Other forms of rapid subsurface flow include pipeflow, flow over bedrock (at depth), and flow over an impermeable layer of clay or fragipan (Anderson and Burt, 1982; McDowell and Wood, 1984; Crabtree and Trudgill, 1985).

The key in the explanation of quickflow response is the size and dynamic nature of the area of the catchment contributing to the flow of water (Dickinson and Whiteley, 1970; Harr, 1977; Taylor and Pearce, 1982; Taylor, 1982; Ward, 1984). The contributing area concept states that the area of the catchment that contributes to the quickflow is determined by rainfall intensity, antecedent wetness conditions, topography, and water table elevation (Taylor and Pearce, 1982) Quickflow yield increases with rainfall and antecedent wetness conditions. Saturated areas around the stream should be the only area where saturation overland flow occurs except when heavy rainfall and antecedent wetness conditions cause more area to be saturated (Sklash and Farvolden, 1979; Taylor and Pearce, 1982; Meyer and Tate, 1983). The expansion of the saturated area is further limited by the soil characteristics and slope of the catchment (Black, 1970; Taylor and Pearce, 1982, Ward, 1984). Subsurface quickflow will occur where saturated overland flow does not, that is in areas where conditions are right for subsurface flow. Soil characteristics and slope again control the appearance of subsurface flow. Antecedent wetness conditions and rainfall determine which form of quickflow will occur in areas not saturated prior to a storm event (Sklash and Farvolden, 1979). Catchments with steep slopes and wide valley bottom wetlands can exhibit both saturation overland flow and subsurface flow while catchments with steep slopes and no wetland or narrow valley bottoms are more likely to exhibit only subsurface flow.

Under baseflow conditions water is supplied to streams by groundwater and soil moisture (Hewlett, 1961; Hewlett and Hibbert, 1963) and transport of DOC to streams is a slow process. The low DOC concentration of groundwater (0.2 - 1.0 mg/l) means that very little DOC is added to streams from terrestrial sources during times of baseflow. In-stream sources are responsible for the majority of DOC during baseflow and the transport of DOC is governed by stream flow. Thurman (1985) discussed the importance of in-stream production of DOC during baseflow conditions and indicated that quiet pools and eddies in the stream channel may become storage areas of DOC.

Transport of DOC to streams can be interrupted or changed by a disturbance within the catchment. Disturbances change the sources, sinks, storage areas of DOC and the hydrologic pathways taken to reach the stream. Removing vegetation by clear-cutting or by other means reduces one of the major inputs of DOC to the catchment. Removal of vegetation also exposes the ground to precipitation and erosion of soil and/or soil compaction cause the pathways of water to be altered. Subsurface flow may be replaced by overland flow, bypassing soil organic horizons. With no input of DOC from covering vegetation, soil organic horizons will be leached and become less and less important as a source of DOC.

Several studies have been conducted to assess the effects of disturbance on catchments (Meyer and Tate, 1983; Tate and Meyer, 1983; Moore, 1989; Moore and Jackson, 1989). Moore (1989) and Moore and Jackson (1989) concluded that disturbance (clearing of vegetation) does cause changes in the DOC concentration in streams and that different degrees of disturbance (complete clearing versus leaving some material behind) cause different DOC concentrations in similar sized catchments.

Meyer and Tate (1983) and Tate and Meyer (1983) investigated the effects of disturbance and successional regrowth of vegetation on DOC concentration in stream water at the Coweeta watershed in North Carolina. They looked at four different catchments with different histories of disturbance and concluded that there were differences in DOC concentration in the streams of the four catchments. They established there was a seasonal pattern to DOC concentration that was similar for all of the study catchments regardless of the type of disturbance.

The transport of DOC is a function of the sources, sinks, and storage areas of DOC and the hydrologic pathways in the catchment. The above review has shown that DOC is released from sources and storage areas in response to precipitation events and water stored in the soil and groundwater. Studies have found that sources, sinks and storage areas remain balanced over long periods of time and DOC concentration in stream water is largely determined by the amount of water available to transport it through the catchment's hydrologic system. The balance is upset when there is some form of disturbance, although as McDowell and Wood (1984) pointed out for Hubbard Brook, this is not always the case. Disturbances tend to alter the sources, sinks, storage areas, and/or hydrologic pathways to a certain degree that either more or less DOC is transported (Wetzel and Manny, 1977; Dahm, 1980; McDowell and Wood, 1984). Meyer and Tate (1983) found that as a catchment recovers from disturbance it will eventually return to the pre-disturbance balance unless the catchment is greatly altered from it's natural state.

DOC VARIATIONS BETWEEN CATCHMENTS

The above discussion has focused on the hydrology of DOC movement from source to stream within a catchment. For well-drained non-wetland catchments, the hydrologic pathways allow DOC to pass into the soil more rapidly, where it can be adsorbed in subsurface soil horizons more readily than in poorly drained or wetland catchments. Poorly drained catchments have impediments to downward movement of water in the soil and therefore, lateral flow occurs bypassing DOC-adsorbing horizons. Wetland areas in poorly drained catchments are major sources of DOC where plants and organic soils are saturated and often waterlogged for periods of time. Well-drained catchments tend to have fewer impediments to water flow than the poorly drained catchments and in soils without DOC adsorbing horizons the DOC-rich water can flow through quickly.

Non-wetland Catchments

The quick passage of DOC through well-drained catchments can be seen in the DOC concentration:discharge relationship during stormflow (Table 4). As the storm event begins the DOC concentration begins to rise. The peak in DOC concentration is reached just after the storm event ceases and there is a rapid decrease back to pre-storm concentration. In

Table 4 it was shown that the DOC concentration was highest on the rising limb of the hydrograph for the non-wetland catchments. DOC is positively related to stream discharge (Q) in the non-wetland catchments as shown in Table 5. The size of the contributing area (i.e. sources of DOC) fluctuates during the storm and follows the same pattern as the DOC concentration (increasing toward the storm peak, then falling as the soil drains).

Table 5

Relationship of DOC to Discharge

Study	Site	Area (ha)	DOC:Q	Level of Significance
Clair & Freedman (1986)	Nova Scotia	87 - 2950	-	0.01-0.001
Foster & Grieve (1982)	England	95.2	+	0.05
Grieve (1984)	Scotland	65	+	0.05
Lewis & Grant (1979)	Colorado	664	+	0.05
Meyer & Tate (1983)	North Carolina	59 - 61	+	0.05
Moore (1989)	New Zealand	1.6 - 8.3	+	0.05
Moore & Jackson (1989)	New Zealand	9.9 - 11.6	+/-	0.01
Mulholland (1981)	North Carolina	800	-/+	0.05
Naiman (1982)	Quebec	2.5 - 198,710	*	0.01

-Note: * negative at high discharge and positive at low discharge (Q).

Physical characteristics of the catchment determine how quickly DOC will reach a stream during storm events. Good drainage and increased slope allow precipitation to infiltrate and percolate downward. The presence of DOC-adsorbing horizons in the soil reduce the amount of DOC that will eventually reach the stream. Source areas in wetland catchments are able to supply more DOC to drainage waters than non-wetland source areas. For these reasons DOC concentration of non-wetland catchments is lower than for wetland catchments. The hydrologic pathways in well-drained soils are related primarily to the slope of the catchment (Reid, 1973; Weyman, 1973; Taylor and Pearce, 1982). Soil drainage is also a function of the slope and the underlying material (Hewlett and Hibbert, 1963; Reid, 1973; Weyman, 1973; Burt, 1979). The absence of wetland, where water tends to stagnate, means that well-drained soils will allow DOC-rich water to pass below the surface and be dealt with in the subsurface pathways.

During baseflow conditions the output of DOC from terrestrial sources is reduced and the majority of DOC is supplied from in-stream sources and storage areas (Thurman, 1985). Subsurface flow from groundwater has very low DOC concentrations (Wallis et al., 1981). The absence of a wetland area that can supply stored DOC to the stream, even during baseflow conditions, is another reason why non-wetland catchments have lower DOC concentrations than wetland catchments.

Wetland Catchments

Hydrologic pathways in wetland catchments are not as clearly defined as in non-wetland catchments. One reason for this is wetland catchments tend to have both saturation overland flow and subsurface flow. The presence of wetland areas that can supply terrestrial DOC in addition to in-stream DOC during baseflow is another reason why wetland catchments have higher DOC concentrations than non-wetland catchments. Beaver ponds and debris dams, common in wetland catchments (Naiman, 1982; Thurman, 1985) are important in-stream sources and storage areas of DOC. Wetland streams tend to be slower moving, a function of lower slope and broader valley bottoms (Taylor and Pearce, 1982), allowing DOC to remain in the stream longer and precipitate into sinks and storage areas. Poorly drained soils tend to have higher DOC concentration due to lateral flow of water in upper soil horizons (McDowell and Wood, 1984).

The response of wetland catchments to storm events points out that there are confusing patterns to DOC concentration in streams flowing from wetland catchments. Some streams show a positive response to increased discharge and others a negative response. The initial response to storms is to produce saturation overland flow over the swampy and boggy soils that are found in wetlands. As the storm passes and percolation of surface water can begin the subsurface component of flow will become the dominant source of water to the stream. The negative relationship between DOC concentration and discharge may be related to the fact that initial flood flow is composed of water bypassing the organic matter by flowing overland. As a storm continues and subsurface flow adds its contribution to flow, DOC concentration will rise. Rising DOC concentration on the rising limb of the hydrograph in some catchments (Meyer and Tate, 1983; Moore, 1989) may be associated with subsurface flow becoming more and more prevalent in storm flow. Other catchments exhibit rising DOC concentration on the falling limb. Once the storm event ends overland flow ceases and DOC concentration begins to return to pre-storm levels.

The differences in stream water DOC concentration between non-wetland and wetland catchments is evidenced by their responses to stream discharge. The differences are functions of the physical characteristics of the catchments. The above introduction and review has pointed out that there are indeed relationships between DOC concentration and the physical nature of a catchment. The next step is to create a model of the physical characteristics of the catchments and use them to predict DOC concentration from a set of test data.

PURPOSE OF STUDY

The above discussion has established the main sources of DOC within a catchment, the main storage areas and the hydrologic pathways that transport DOC to steams. However, there have only been a limited number of studies that have dealt with more than one catchment at a time. Moeller et al. (1979) have conducted the only study on establishing what physical characteristics of a catchment control variations in DOC. They determined that stream link magnitude (a function of the number of channels coming into a stream), watershed area, and discharge explained most of the variation in DOC export in several different physiographic regions in the USA. They also established that there were seasonal patterns to DOC export which varied between different regions, but failed to determine whether other physical factors may have been responsible for the variations in DOC concentration within the streams they investigated. Furthermore, their analyses were biased because of a high degree of multicollinearity in the data set.

The main focus of this study is to determine what physical characteristics of catchments are associated with stream DOC concentrations by examination of eight small catchments in the Eastern Townships, four of which contain significant areas of wetland and four which do not. Based on these relationships, a predictive model of stream

DOC concentration will be created for a wider range of catchments.

Five questions have been formulated to establish links between the DOC concentration of stream water in the study catchments and the physical characteristics of the catchments. The first four questions are concerned with variations of DOC concentration within each catchment and between the catchments. The fifth question is concerned with the validation of the predictive model.

The five questions are:

1) are there differences between the DOC concentration of streams draining wetland catchments and those draining non-wetland catchments?

2) for non-wetland catchments can percentage forest be used as an indicator of DOC concentration?

3) is DOC concentration related to discharge and are there differences between wetland and non-wetland catchments?

4) do wetland catchments show different seasonal variations in DOC concentration than non-wetland catchments?

5) can DOC concentration, in a wide range of catchments, be predicted using simple physical characteristics of the catchments?

CHAPTER 2

METHODOLOGY

Catchment Selection

The main study area includes eight catchments (Table 6, nos. 1-8) which make up part of the Rivière Noire-Rivière Yamaska catchment located approximately 100 km east of Montreal in the vicinity of Valcourt, Quebec 45° 18'N, 72° 12'W. The Eastern Townships provide a mixture of land uses and forest cover, varied slopes, different soils, and different sized wetlands. The eight catchments were chosen based on their size (3 - 9 km^2) and land use.

The soils in the area are a mixture of Brunisols, Podzols, and Gleysols with several wetlands containing accumulations of peat to depths up to 8 metres in places. Soil data were obtained from county soil surveys at the scale of 1:63360 (Cann et al., 1947) and the Canadian System (Canada Department of Agriculture, 1978) was the basis for classifying the soils (Table 7). The soils are derived from metamorphic (schist, slate and sandstone) parent material and there is a layer of glacial till over the whole area. There are areas of open rough stony land where the country rock shows through the till. There are sand deposits scattered around the area which are associated with eskers and sand dune formations from the last ice age.

Topographic maps and aerial photographs were used in determining data on land use coverage. Descriptions of each of the eight catchments are given below. A BASIC program (Stolk and Ettershank, 1987) for estimating the area of irregular shapes was used in measuring the

TABLE 6

Physical Characteristics Of The 42 Catchments

	CATCHMENT #	WETLAND (%)*	AREA (km^2)	SLOPE (m/km)	DRAIN-AGE	FOREST (%)+
	1	0.0	5.2	25.5	4.0	42.9
Original	2	0.0	3.0	24.5	2.5	20.0
Eight	3	0.5	3.5	23.2	3.0	69.7
Upland	4	0.5	7.0	30.5	3.0	75.9
Group	5	15.0	8.5	24.0	1.0	60.0
	6	23.0	7.5	10.9	1.5	84.9
	7	31.1	8.7	18.9	1.5	83.5
	8	68.8	9.0	8.4	1.0	92.9
	9	0.0	6.5	37.6	2.5	81.4
	10	0.0	2.3	45.7	2.0	11.1
	11	0.0	3.1	45.4	3.0	63.9
Extra	12	0.0	3.2	30.5	2.5	60.0
Upland	13	0.7	37.2	49.5	4.5	88.0
Group	14	0.8	13.3	29.7	1.5	63.0
	15	1.0	4.1	28.0	3.0	60.0
	16	2.2	5.0	14.6	3.8	60.0
	17	4.5	7.0	30.5	3.0	75.9
	18	5.8	19.4	18.5	2.0	80.0
	19	6.6	17.0	11.0	2.0	75.0
	20	8.8	1.7	45.1	3.0	20.0
	21	11.7	8.7	30.8	4.0	55.0
	22	17.6	4.3	44.9	2.0	87.2
	23	21.0	6.0	36.1	2.5	69.9
	24	44.0	0.6	7.1	1.0	94.7
	25	0.0	5.2	2.4	1.5	7.5
	26	2.0	4.6	2.5	2.5	15.0
Lowland	27	10.4	25.5	12.5	3.8	55.0
Group	28	21.4	4.4	6.6	3.5	40.0
	29	24.3	1.8	5.0	1.3	39 0
	30	25.0	0.6	7.0	2.6	35.0
	31	25.6	5.2	6.3	0 0	49.9
	32	28.5	4.9	4.4	2.7	74.9
	33	29.0	8.3	1.3	1.5	49.9
	34	33.0	8.7	2.7	1 3	20.0
	35	38.5	11.0	1.3	1.3	65.0
	36	47.0	4.0	4.2	1.0	75.0
	37	51.3	0.0	1.3	1.0	40.0
	38	52.8	4.0	7.4	2.8	55.0
	39	55.9	8.8	5.5	1.0	69.9
	40	56.1	31.6	2.4	0.0	55.1
	41	56.4	4.2	1.8	1.0	70.0
	42	79.0	6.2	1.1	0.0	55 0

Note: *=Percentage wetland; +=Percentage forest includes all forested land in catchment. The Extra Upland and Lowland groups are dealt with in Chapter 4.

area of each catchment. Catchment type was determined by the presence/absence of wetlands (i.e. bogs, fens, swamps, beaver ponds) in each catchment Four catchments contained 15 to 69% wetland while the other four catchments had less than 0.5% occupied by wetland. For convenience the eight catchments have been abbreviated by numbers 1-8 as follows:

Lawrenceville		1
Eleventh Rang		2
Warden		3
Bonsecours		4
Valcourt 2	*	5
Wilson Pond	*	6
Sixth Rang	*	7
Bethanie	*	8

Note: * - wetland catchments.

Farming activity is present in seven of the catchments with hay and corn being the main crops Many farms were primarily concerned with livestock production and dairy activities. During the study season, many fields had been left fallow and others appeared to be abandoned.

Mixed deciduous (birch, maple, alder, aspen, ash, poplar) and coniferous (spruce, cedar, tamarack, and fir) forests dominate with more concentration of coniferous trees in wetland catchments around bogs and swamps. Bogs contain low shrubs and herbaceous plants as well as 3-5 m high tamarack trees. Other bog lands are covered with rushes and tall grasses with some shrub growth. The non-wetland catchments are steeper sloped and have more variety of deciduous trees, contain more farming activity and more open land than the wetland catchments. Wetland streams are slow moving and the channels contain grass and weeds, while non-wetland catchment streams were rocky and more turbulent. Alders are

TABLE 7

Catchment	Soil Group(s)	% of Area	Parent Material
1	Blandford Loam	92	Schist
	Gleyed Eutric Brunisol		
	Brompton Sandy Loam	8	Slate & Sandstone
	Humic Gleysol		
2	Blandford Loam	65	Schist
	Gleyed Eutric Brunisol		
	Brompton Sandy Loam	35	Slate & Sandstone
	Humic Gleysol		
3	Blandford Loam (Shallow)	90	Schist
	Dystric Brunisol		
	Rough Stony Land	8	Schist
	Marsh	2	-
4	Blandford Loam	55	Schist
	Gleyed Eutric Brunisol		
	Brompton Sandy Loam	15	Slate & Sandstone
	Humic Gleysol		
	St. Francis Sandy Loam	2	Slate & Sandstone
	Humo-Ferric Podzol		
	Woodbridge Loam	8	Schist
	Gleyed Dystric Brunisol		
	Rough Stony Land	17	-
	Undifferentiated Alluvium	3	Recent Alluvium
5	Blandford Loam (Shallow)	45	Schist
	Dystric Brunisol		
	Brompton Loam	30	Slate & Sandstone
	Humic Gleysol		
	Racine Sandy Loam	10	Slate & Sandstone
	Humo-Ferric Podzol		
	Peat and Marsh	15	-
6	Blandford Loam (Shallow)	18	Schist
	Dystric Brunisol		
	Brompton Loam	60	Slate & Sandstone
	Humic Gleysol		
	Peat and Marsh	22	-
7	Blandford Loam (Shallow)	69	Schist
	Dystric Brunisol		
	Brompton Sandy Loam	3	Slate & Sandstone
	Humic Gleysol		
	Rough Stony Land	8	-
	Peat and Marsh	20	-
8	Blandford Loam (Shallow)	7	Schist
	Dystric Brunisol		
	Blandford Loam	8	Schist
	Gleyed Eutric Brunisol		
	Brompton Loam	20	Slate & Sandstone
	Humic Gleysol		
	Racine Sandy Loam	4	Slate & Sandstone
	Humo-Ferric Podzol		
	Peat and Marsh	61	-

found along almost every stream except on farm land where the banks of streams have been cleared for animals to reach the water.

Precipitation data supplied by Environment Quebec are based on a farm-based meteorologic station near Bonsecours. The station is attended twice a day and rainfall and snowfall are recorded separately. The station operates all year and a continuous record of precipitation from April to November 1988 was available.

To the original 8 catchments were added a further 34 catchments (Table 6, nos. 9-42) located south and south east of Montreal in a predominantly agricultural area of the Saint Lawrence Lowland and east of Montreal in the Appalachian Upland. Criteria for selection of the 34 catchments were: a) size, b) range of land use (wetland area), c) ease of access to outlet, and d) range of soils and geomorphic settings. Of the 34 catchments, the majority contain wetlands or former wetlands, some of which have been drained to enable farming. Slopes were relatively shallow in the Lowland catchments and steep in the Upland catchments. The 34 catchments range in size from 0.5 km^2 to 35 km^2 and were selected to represent a wide range of wetland characteristics (0.0 to 79%). The 34 catchments were sampled four times (August, September, October, and late November) in order to help establish a seasonal pattern to DOC concentration.

Study Area Catchment Descriptions

Non-wetland Catchments

The four non-wetland catchments varied in land use (percentage forest versus percentage developed land). Two of the catchments (3 and

4) are predominantly forested while the other two are more developed. Table 6 lists the physical characteristics of each catchment and Table 7 lists the soils.

Catchment 1 is a mixed forested-agricultural catchment (predominantly agricultural) underlain by Blandford loam and Brompton sandy loam. An even mixture of coniferous and deciduous trees are found in the forested areas, which accounts for about half of the land use in the catchment. Pasture land, which accounts for the other half of the land use, supports several small dairy herds. There is evidence of small scale logging activity in the catchment. The whole catchment is gently rolling and the steepest slopes are found near the sampling point.

Catchment 2 is a mixture of forest, crop land and pasture (approximately 80% open pasture) underlain by Blandford loam and Brompton sandy loam. Deciduous trees dominated the forested land in the catchment. Crop land in the catchment is devoted entirely to corn production for use by the local dairy herds and pasture land is used for grazing cattle. The catchment is gently rolling throughout.

Catchment 3 is a mainly forested catchment underlain by Blandford loam (shallow phase) and Woodbridge loam. The land is fairly bouldery and hilly. There are several small farms in the catchment which are predominantly pasture land and several corn fields. Forested areas are predominantly covered in deciduous trees with stands of coniferous (spruce mostly) trees in the wetter parts of the catchment.

Catchment 4 is a mixed forested-agricultural (predominantly forested) catchment underlain by Blandford and Woodbridge loams, Brompton sandy loam, and alluvial soils (undifferentiated). Agriculture is entirely given to pasture. Forested land is dominated by deciduous species with coniferous species found only on wetter sites near the stream. There is a small marshy pond in the centre of the catchment that is frequented by water fowl. The catchment is fairly steep sloped throughout.

Wetland Catchments

The four catchments with wetland components differ from one another in the type of wetland present in each catchment. Table 6 lists the physical characteristics of each catchment and Table 7 lists the soils.

Catchment 5 is composed of bog, and farm land and forested areas underlain by Blandford shallow loam, Brompton sandy loam, and Racine sandy loam. Bog soils are Humic Gleysols with accumulations of peat along the stream. The surrounding farm land is a mixture of crop (corn) and pasture. Forest consists mainly of tamarack and spruce in the low land, while higher ground is covered almost exclusively by maple, beech, and birch.

Catchment 6 is composed of a large pond (Wilson Pond), peat bogs, and several beaver ponds surrounded by two sandy loams. The two major soil types in this catchment are the Blandford sandy loam which is a Dystric Brunisol derived from schistose material and Brompton sandy loam which is a Humic Gleysol that is a reworked sandy loam derived largely from slate and sandstone material. The surrounding land is a mixture of forest and pasture with several small fields used for crops. Forest is predominantly birch, maple, and poplar on higher ground and spruce, balsam fir, and cedar on wetter ground. Speckled alder is prominent along the stream channel. Bog areas are covered with tamarack, shrubs, and herbaceous plants and are surrounded by coniferous trees along the bog fringe.

Catchment 7 is composed of swamp, peat bog, and several beaver ponds contained in a gently sloping catchment surrounded by a Dystric Brunisol (Blandford loam, shallow phase) that is derived from schistose parent material. The swamp land has been described as thin organic accumulations over the mineral soil base (Cann et al., 1947). There is rough stony land that consisted of schist and other metamorphic rocks and boulders. The surrounding land is predominantly forested in spruce, cedar, fir, alder, maple, and birch. Deciduous species are found on drier sites than coniferous species. Bog and swamp areas are covered with tamarack, spruce, cedar, shrubs, grasses and speckled alder. Areas flooded by beaver ponds originally were covered by a variety of tree species. Little cleared farm land is present in this catchment.

Catchment 8 is composed of a large bog which is surrounded by a Dystric Brunisol, Humic Gleysol and a Humo-Ferric Podzol. Blandford loam is as described above. Brompton sandy loam (described above) and Racine sandy loam, a Podzol, are of similar origin. The bog and swamp soils consist of Humic Gleysols and Mesisols. The surrounding land is heavily forested with several small pastures and a cattle farm. Forest consisted of a mixed coniferous and deciduous species while bog areas are dominated by tamarack and small trees, shrubs and sphagnum. There are large stands of immature birch in the catchment. Coniferous species consist mainly of cedar, balsam fir, and spruce.

Sampling Scheme

Up to 500 ml of water from the stream draining each of the 8 main catchments was collected at weekly intervals from April 20 to November 30, 1988. As sampling within the stream cross section revealed negligible variation in DOC concentration, the samples were taken from the central portion of the stream channel. A current meter was used from April to late June to measure velocity in the culvert and bridge cross sections to provide discharge measurements. At other times, a float-velocity method was utilized to estimate discharge using a correction factor of 0.9 of the surface velocity (Moore, R. D., pers comm.).

Stage height was measured from stakes driven into the stream bed. A Belfort continuous strip chart water level recorder was set up on Catchment 7 (Sixth Rang bridge); several occurrences caused the record to be discontinuous. The first occurred in June when a local resident drove a bulldozer into the stream to clear out the grass in order to make his back yard more appealing. The second occurred in July when someone tampered with the measuring device. The third occurred in November when someone blew up a beaver dam that was just upstream causing a flood.

Chemical Analysis

The stream water samples were filtered through Whatman GF/C paper and stored at 2-4°C. Absorbance at 330 nm was determined on an LKB Biochrome 4050-011 Ultrospec spectrometer. Aliquots ranging in size from 5 to 100 ml were placed into 250-500 ml flasks and evaporated in an oven at 95°C. After evaporation, the residue was dissolved in a mixture of 10 ml 0.02N $K_2Cr_2O_7$ and 25 ml $H_2SO_4/H_3PO_4/AgSO_4$ and transferred into tubes for digestion for 3 hours at 100°C in a Technicon BD-40 Block Digester. After digestion and cooling, samples were transferred to conical flasks, diluted with 100 ml distilled water and titrated with an 0 1N NH_4FeSO_4 solution to which 1.0 ml of 0.16% barium diphenylamine sulphonate indicator was added (Moore, 1985, 1987).

A secondary reason for measuring absorbance was to check a simple method for estimating DOC concentration based solely on absorbance, removing the need to use further chemical analysis. The equation for the regression is:

$$DOC = 2.82 + 69.29(X)$$

X = absorbance at 330 nm, 1cm cell

$r^2 = 0.85$ Standard error = 1.86

n = 240 Significance Level = 0.0001

Mean DOC = 16.64 Standard Deviation = 5.21

These figures fall within the range of values given by Moore (1987) in his Table 2 (p.588) for river and peat water samples. Results suggest that water colour can be used as a simple, effective surrogate for stream DOC concentration over wide ranges of geochemical conditions.

Electrical conductance (Ec at 25° C) and pH measurements were made on a Yellow Springs Instruments Model 32 Conductance Meter and a Fisher Accumet ph Meter Model 210. Cations (Ca, K, Na, Mg), iron and aluminum were determined using atomic absorption spectrophotometry and anions (Cl^-, SO_4^-, NO_3^-) through ion chromatography. Carbonate (CO_3) concentrations were determined by a gravimetric titration procedure (Environment Canada, Water Resources Branch). Electrical Conductance, pH, cation and anion data are discussed in Chapter 3.

Statistical Analysis

The statistical analysis techniques used in this study were all taken from published sources and computer tape libraries available from SAS (SAS, 1982, 1985) and LOTUS 1-2-3 (Ewing et al., 1987). The data were analyzed using scatter plots, simple diagnostic tests, and simple and multiple linear regression using the variables listed below. Chapters 3 and 4 include detailed sections on the statistical procedures used on the two data sets collected for this project.

MODEL DATA

The data for the predictive model consist of the dependent variable DOC concentration and five independent variables, including percentage wetland, percentage forest land, slope, area, and drainage.

Dependent Variable

DOC concentration of streams

DOC concentration (mg/l) was determined by chemical analysis of each sample, as described above.

Independent Variables

Percentage Wetland

All types of wetlands (swamps, bogs, beaver ponds, marsh) were included, gathered from topographic and soils maps and aerial photographs.

Percentage Forest

The total forested area of the catchment gathered from topographic maps and aerial photographs.

Area

Catchment area, in square kilometres, was determined from topographic maps and a grid overlay.

Slope

Mean or average slope, in metres/kilometre, was calculated by a formula that determined the average slope of the catchment from the watershed boundary to the stream channel (Rasmussen, pers. comm.).

$$\text{Slope} = (\Delta\ \text{Altitude})/\sqrt{(\text{Area}/\pi)}$$

Change in elevation (Δ Altitude) was determined as the average change in elevation from the catchment boundary to stream edge measured on a topographic map.

Drainage

Drainage was based on the drainage characteristics of all soils in the catchment, obtained from County Soil Survey Maps. A set of dummy values were assigned to the qualitative descriptions of drainage weighted on percentage area of soil type in each catchment. The data appears as:

Value	Description
0	Very poor (très mauvais)
1	Poor (mauvais)
2	Imperfect (imparfait)
3	Moderate (moderate)
4	Good (bon)
5	Excellent (excessif)

DOC:DISCHARGE DATA

Other data collected during the study period was used to study the relationship of DOC concentration to stream discharge.

Discharge

Discharge (m^3/s) was determined by float-velocity or current meter method.

Date

The Julian date was used for this variable.

Precipitation

This variable was defined as the amount of precipitation (mm) that fell at a farm-based meteorological station (listed above) one week prior to sampling. Snow in April, October, and November was converted to water equivalent depth by dividing the snow depth by a factor of 10. The data was obtained from Environment Quebec, Ste. Foy, Quebec. These data were used to help establish the role of storm events in DOC transport in the study catchments.

CHAPTER 3

INTRODUCTION

Establishment of the physical characteristics associated with DOC concentration of stream water led to the creation of a linear regression model that was tested on a wide variety of catchments. The above review indicated that there were differences in DOC concentration of streams draining wetland catchments and streams draining non-wetland catchments. This chapter deals with the results from the data analysis and model building procedures, as well as the water chemistry analyses

DATA ANALYSIS

The five questions proposed in Chapter 1 will be discussed separately below. Each sub-section will discuss testing procedures, and give conclusions on the findings. APPENDIX A (Tables 1-3) lists the data used in this chapter.

Question 1

The first question dealt with determination of differences in DOC concentration of streams in two groups of physically different catchments. The two groups of catchments consist of a) four with 15, 23, 31, and 68% wetland area, and b) four with 0, 0, 0 5, and 0.5% wetland area. A non-parametric NPAR1WAY procedure (SAS, 1982) was used for the testing the null hypothesis that the median DOC concentration of the two sets of data are equal and that they came from the same population. The exact test used by the NPAR1WAY simulates a Mann-Whitney U-test and prints a simulated chi-square value for hypothesis testing (SAS, p. 206, 1982). The data of median and mean DOC concentration appear in Table 8.

TABLE 8

Catchment	Median DOC	Mean DOC
1	3.8	3.9
2	3.4	3.5
3	6.6	7.2
4	3.6	3.8
5 *	14.7	14.5
6 *	31.9	32.1
7 *	21.8	21.9
8 *	39.8	40.0

Note: *=wetland catchments; all values in mg/l.

APPENDIX B, Table 1 shows the results of the NPAR1WAY procedure on the two sets of data. Degrees of freedom were calculated (SAS, p. 208, 1982) as the number of levels of the class minus 1 (for this test DF=1). Based on the results of the test at 0.02 level of significance (simulated chi-square value = 5.33) the null hypothesis was rejected meaning that there was a significant difference in the DOC concentration of stream water flowing from the wetland catchments versus the non-wetland catchments

Question 2

The second question was concerned with using percentage forest in non-wetland catchments as a simple predictor of DOC. For this test percentage forest values from the 4 original non-wetland catchments were used. The data are summarized in Table 9.

TABLE 9

Mean Annual DOC and % Forest for Non-wetland Catchments

Catchment	Mean DOC (mg/l)	Forest (%)
1	3.9	43
2	3.5	20
3	7.2	70
4	3.8	76

The strength of the relationship is poor and percentage forest is not a good predictor of mean DOC for the non-wetland catchments. From Table 9 it can be seen that Catchment 3 has almost twice as high a concentration of DOC than the other catchments and about 2 to 3 times as great a percentage of forest land than two of the other catchments. Catchment 4 has about the same percentage forest but the DOC concentration is about half that of Catchment 3 and similar to the Catchments 1 and 2.

The reason why Catchments 3 and 4 differ in DOC concentration while having similar percentage forest may be a function of vegetation type in the catchments. Catchment 3 has more coniferous vegetation and the understorey is covered in mosses and ferns while Catchment 4 is predominantly deciduous and the understorey is fairly clear of growth. Data on differences in DOC concentration from different vegetation types confirm that coniferous species (common in this area) produce more DOC than deciduous species (Dalva, in press) Catchment 1 is a mixture of coniferous and deciduous species while deciduous species dominate the small areas that are covered in forest in Catchment 2.

Question 3

The third question was related to the effect of stream discharge on DOC concentration. For the whole study period there was an overall fair to poor relationship between DOC concentration and either discharge or ln discharge. Non-wetland catchments had more significant results than the wetland catchments. Table 10 summarizes the results from the regression of DOC concentration and Discharge.

TABLE 10

Regression Equations For Wetland And Non-wetland Catchments

Catchment	Equation	r^2	S.E.	Sig. Level
1	DOC = 3.36 + 5.39(X)	0.31	0.25	0.0009
2	DOC = 2.95 + 15.28(X)	0.43	0.20	0.0001
3	DOC = 6.85 + 5 45(X)	0 15	0.43	0.0263
4	DOC = 3.04 + 6 05(X)	0.52	0.21	0.0001
5	DOC = 14.06 + 1.55(X)	0.00	1.43	0.7572
6	DOC = 30.70 + 11.71(X)	0.04	1.72	0.2507
7	DOC = 22 57 - 4.81(X)	0.01	1.48	0.5187
8	DOC = 42.51 - 25.77(X)	0.05	2.60	0.2348

Note DOC is in mg/l; X is discharge in cubic metres per second.

The signs of the slope coefficients for all non-wetland and the two wetland catchments (5 and 6) were positive, therefore there was direct positive relationship between the DOC concentration and discharge. The r^2 values for the wetland catchments were all very low 0.00 to 0 05 while the non-wetland catchments were higher 0.15 to 0.52 The signs of the slope coefficients for two of the wetland catchments (7 and 8) were negative meaning a direct negative relationship between DOC concentration and stream discharge, however the strength of the relationship is very weak or non-existent for all wetland catchments. Figures 1-8 show the relationship between DOC concentration and discharge for each of the eight catchments.

Figure 1

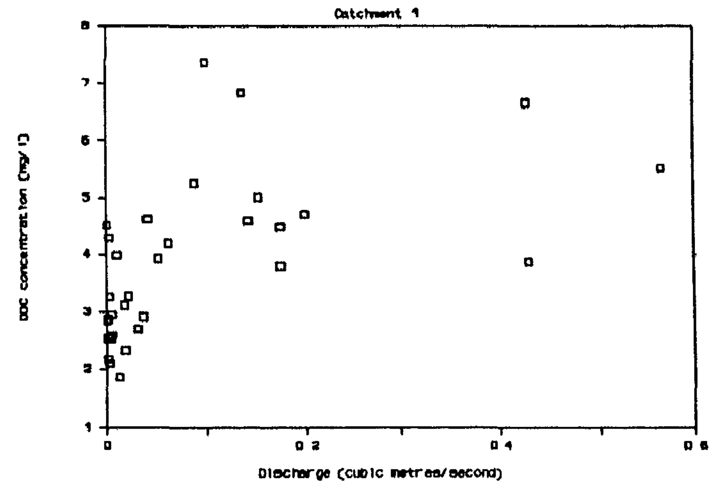
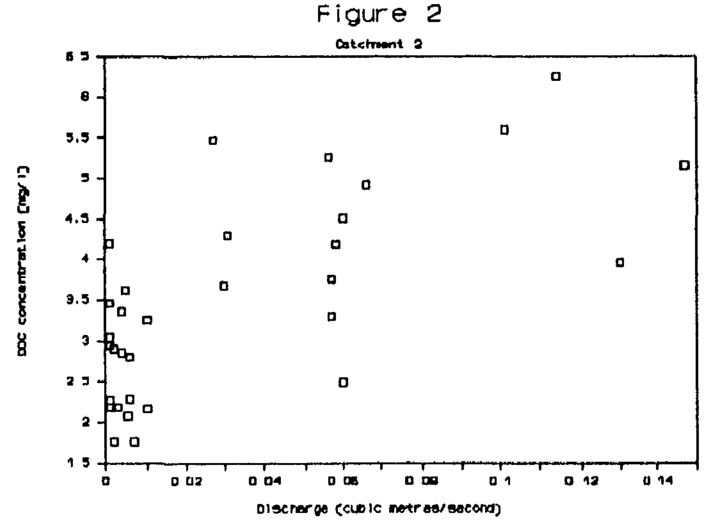


Figure 2



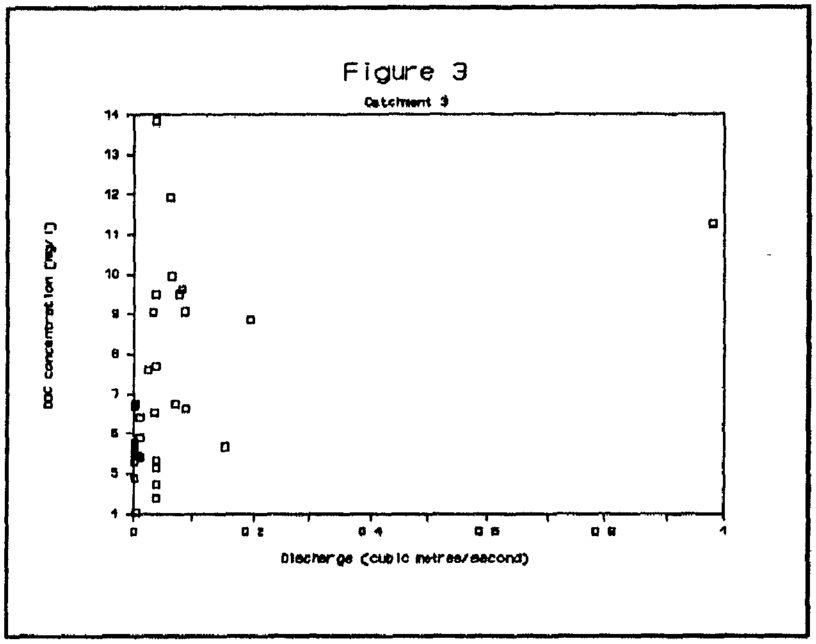


Figure 3
Catchment 3
DOC concentration (mg/l)
Discharge (cubic metres/second)

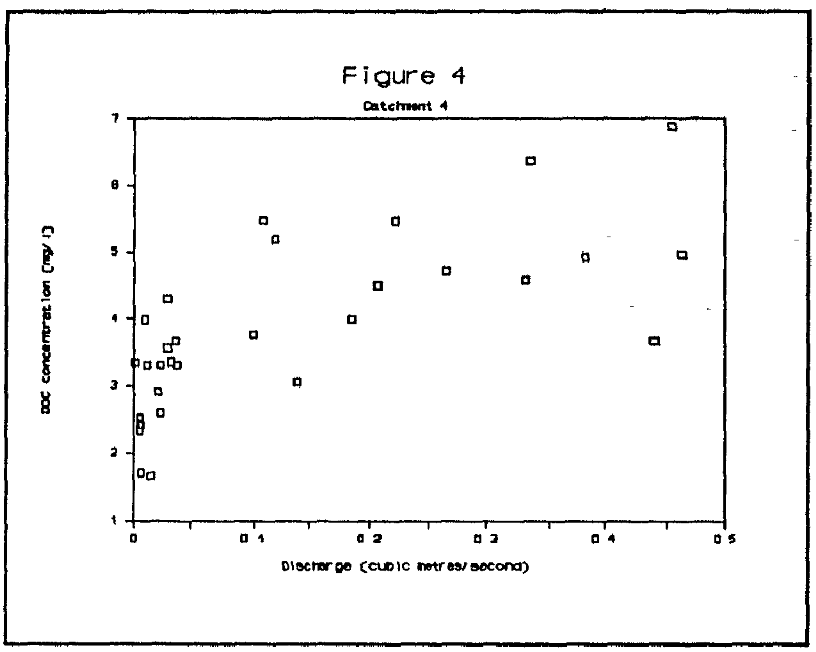


Figure 4
Catchment 4
DOC concentration (mg/l)
Discharge (cubic metres/second)

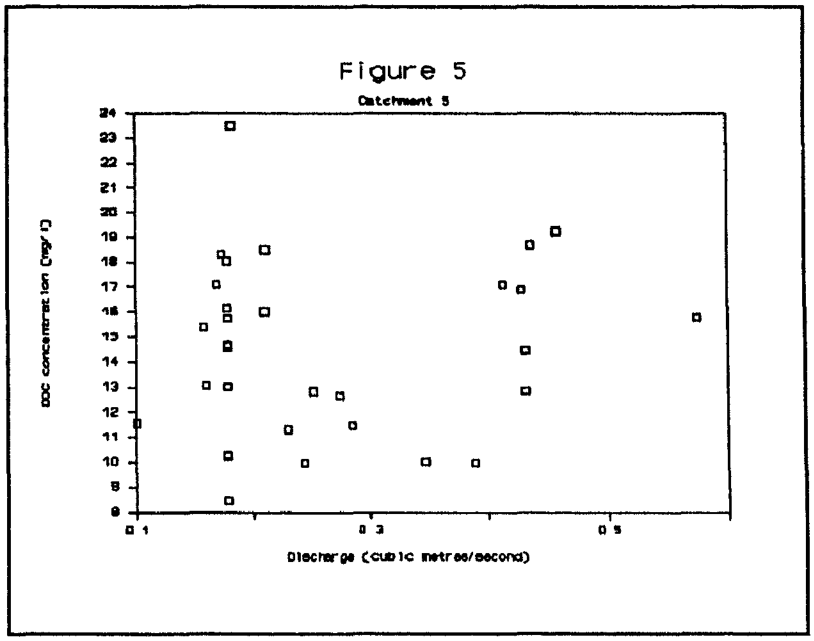


Figure 5
Catchment 5
DOC concentration (mg/l)
Discharge (cubic metres/second)
0.1
0.3
0.5

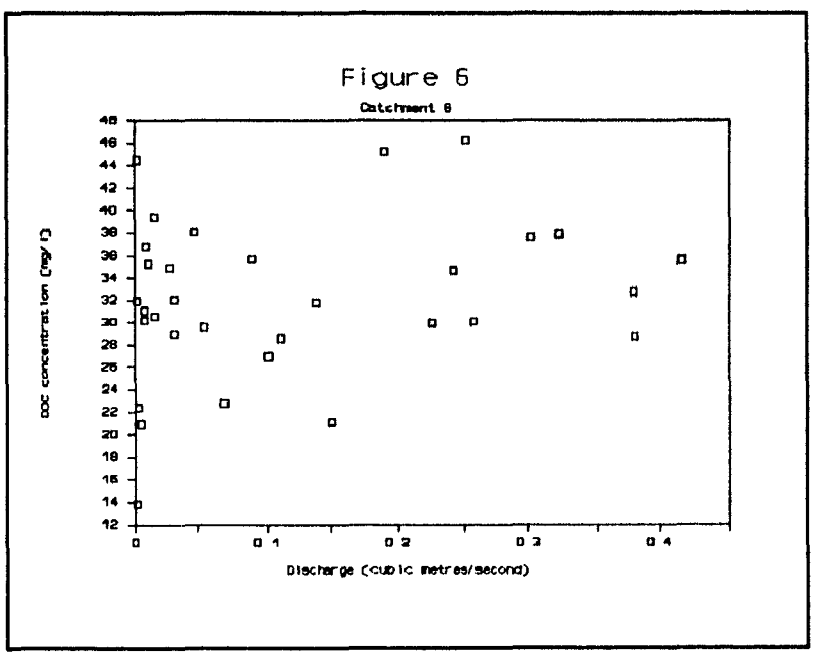


Figure 6
Catchment 6
DOC concentration (mg/l)
Discharge (cubic metres/second)
0
0.1
0.2
0.3
0.4

Figure 7

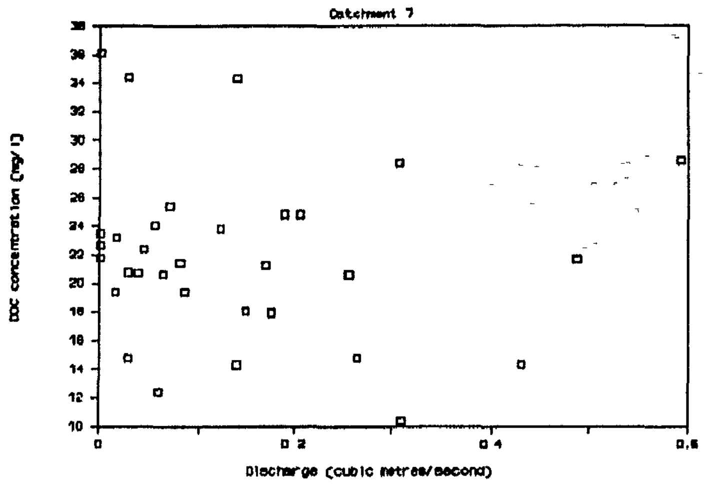
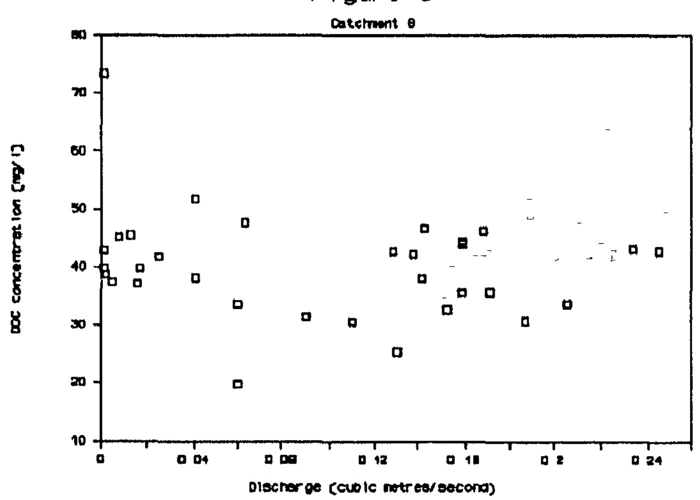


Figure 8



The data show that discharge is not a good indicator of DOC concentration for wetland catchments, but in certain non-wetland catchments it accounts for a fair amount of the variation in DOC concentration. Using ln discharge and ln DOC concentration improves the r^2 and SEest for the non-wetland catchments, but does not improve the relationship for the wetland catchments. Table 11 lists the equations for the transformed data. Figures 9-16 show the relationship between ln(DOC concentration) and ln(discharge) for each of the eight catchments.

TABLE 11

Regression Equations For Wetland
And Non-wetland Catchments

Catchment	Equation	r^2	S.E.	Sig. Level
1	LDOC = 1.73 + 0.11(X)	0.42	0.11	0.0001
2	LDOC = 1.83 + 0.15(X)	0.53	0.12	0.0001
3	LDOC = 2.33 + 0.10(X)	0.28	0.12	0.0036
4	LDOC = 1.83 + 0.19(X)	0.66	0.08	0.0001
5	LDOC = 2.69 + 0.15(X)	0.00	0.15	0.7393
6	LDOC = 3.54 + 0 03(X)	0 05	0.08	0.2395
7	LDOC = 2.90 - 0.06(X)	0.09	0.10	0.1078
8	LDOC = 3.59 - 0.02(X)	0.01	0.09	0.5354

Note: LDOC is ln(DOC concentration); X is ln(discharge).

The lack of a negative relationship for wetland catchments 5 and 6 may be related to the presence of a several large beaver ponds in catchment 6 and slow moving water in catchment 5. The pond and sluggish water act as retention devices (Naiman, 1982) which can cause precipitation of suspended particles, with DOC molecules attached to their surfaces, onto the stream bed in low velocity streams.

Figure 9

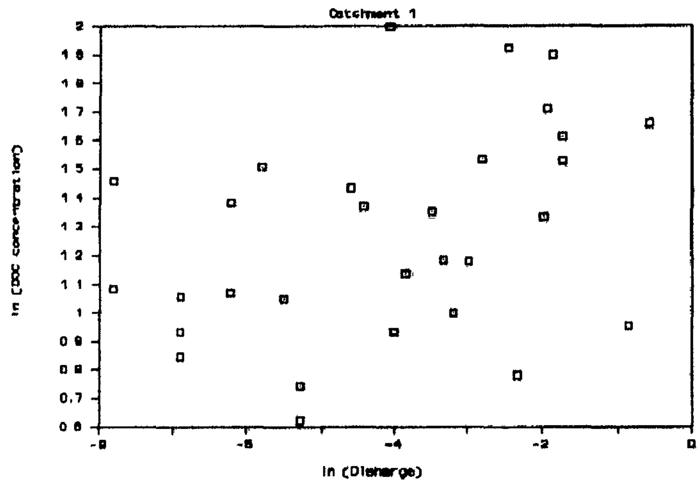


Figure 10

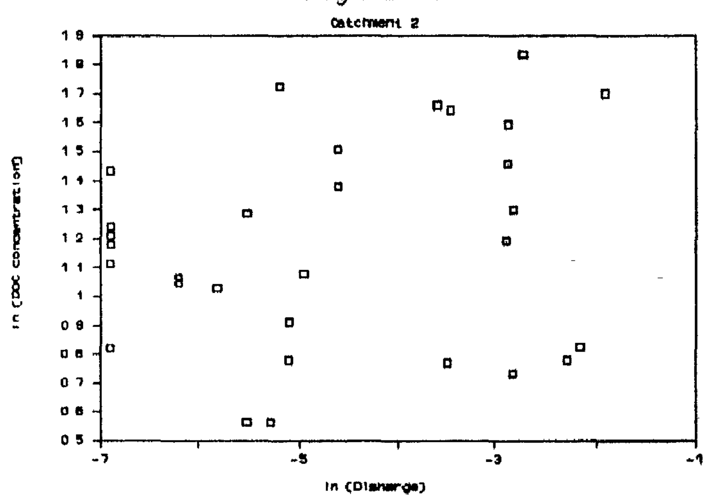


Figure 11

Catchment 3

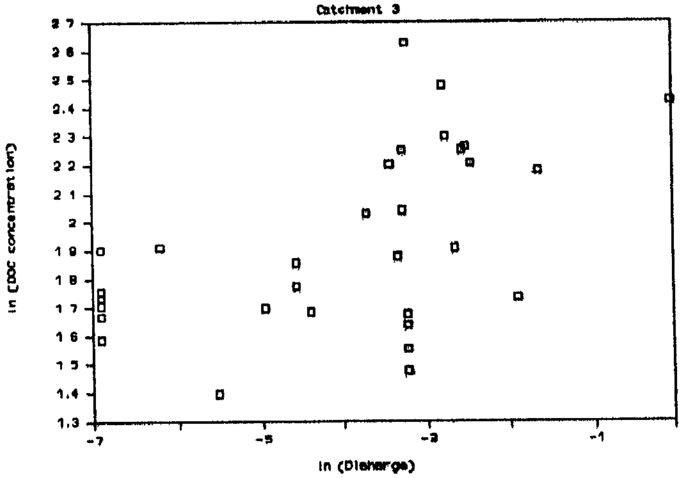


Figure 12

Catchment 4

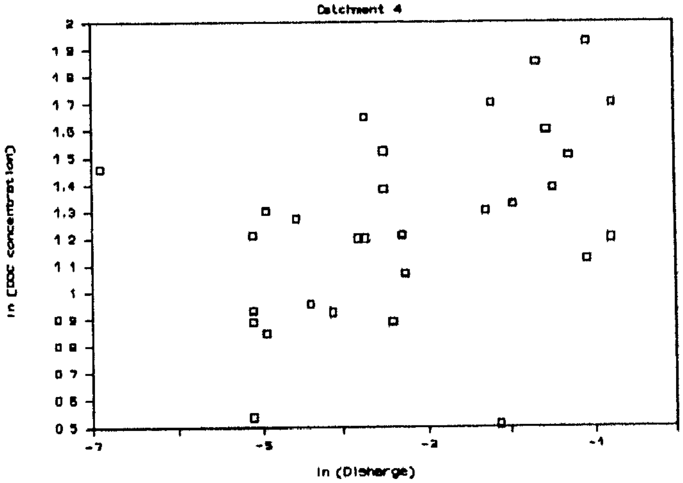


Figure 13

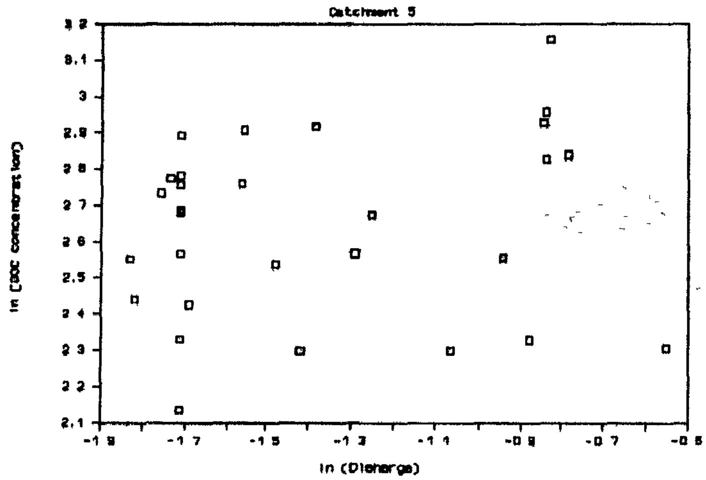
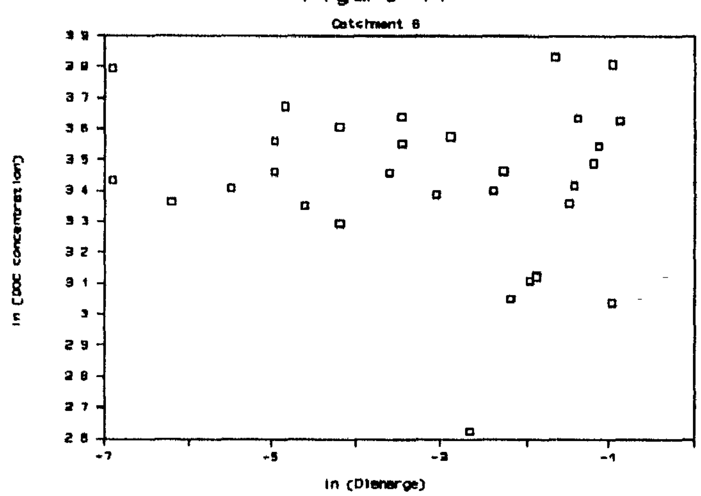


Figure 14



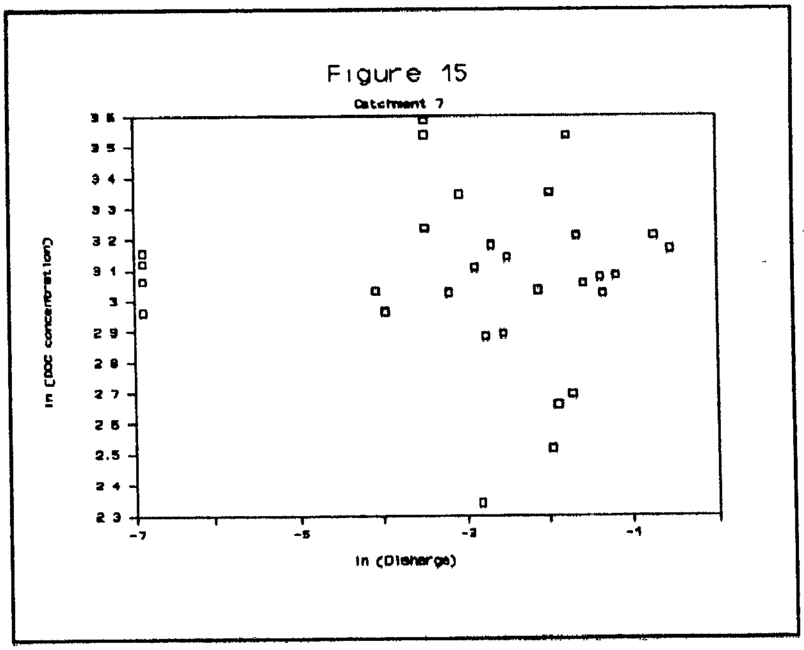


Figure 15
Catchment 7
ln (DOC concentration)
ln (Discharge)

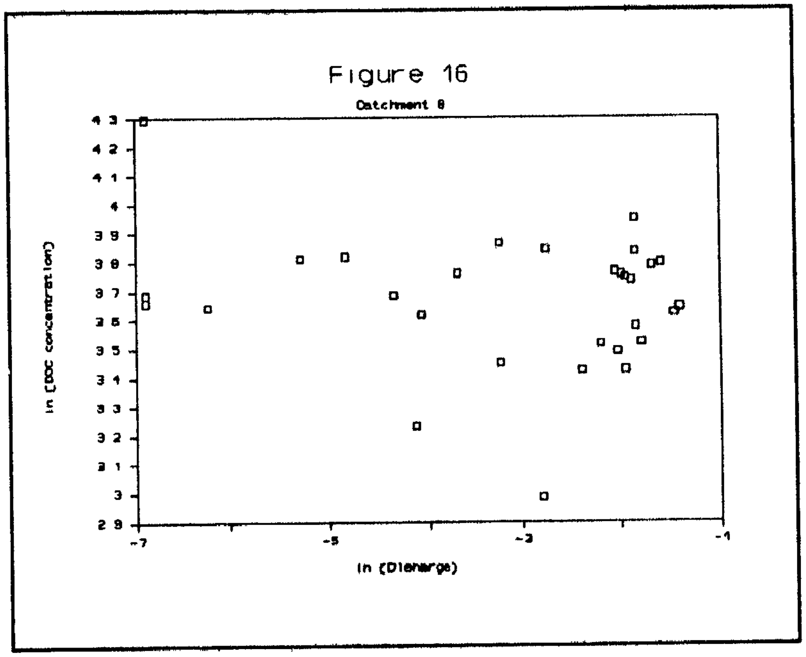


Figure 16
Catchment 8
ln (DOC concentration)
ln (Discharge)

Transforming the data for DOC concentration and discharge improved the r^2 values and lowered the SEest for each of the catchments. The natural log transformation normalized the data and improved the significance of the relationship.

In order to determine where DOC is coming from in a catchment, samples of stream water from Catchments 3 and 7 were taken (in July and September) at varying intervals upstream from the regular sampling points. Figures 17 and 18 show the stream DOC concentration from the weir to several points upstream. Catchment 3 has a second order stream flowing past the regular sample point. The two first order streams that flow into it were sampled above the points where they intersect the main channel Another sample was taken below the intersection of the two streams and upstream from the regular sample point. The four points show that more DOC was being delivered by one of the smaller streams and that the DOC concentration decreased downstream. The stream with the higher DOC concentration flowed out of a forested areas dominated by coniferous trees, ferns and mosses. The stream with lower DOC concentration flowed out of a forested area with more of a mixture of tree species and several open fields.

Catchment 7 had a beaver dam 250 metres upstream from the regular sample point which did not affect the stream DOC concentration greatly in July, but by September the DOC concentration in the beaver pond (along the side and directly behind the dam) was much higher than in the flowing stream both above and below the pond. It would appear the dam acts as a retention device (Naiman, 1982) for DOC. After the dam was blown up (November) stream DOC concentration returned to pre-dam levels.

Figure 17

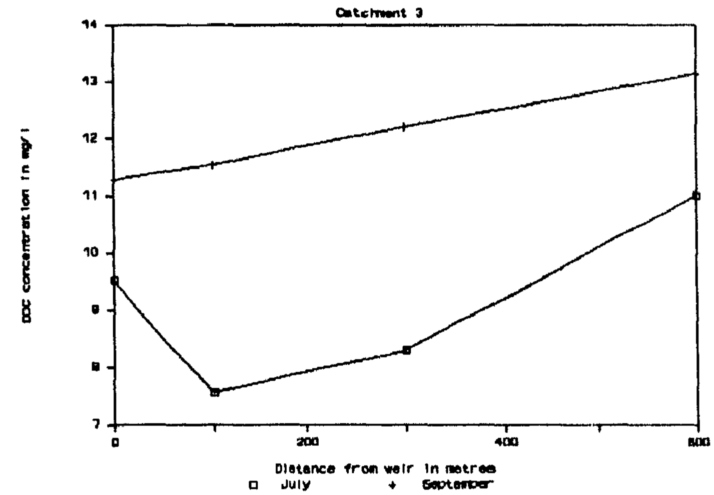
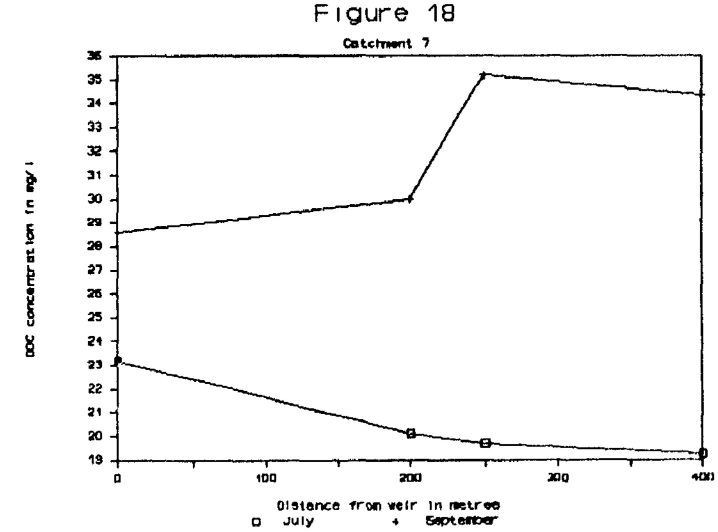


Figure 18



Decreasing DOC concentration downstream meant DOC was being produced in the headwaters and was being either consumed by in-stream processes, precipitated directly onto the stream bed, adsorbed by ionic compounds and precipitated onto the stream bed, or released into the atmosphere as CO_2 gas (Thurman, 1985). Increasing DOC downstream may be related to retention devices, inputs of DOC-rich water from a tributary, water passing through organic matter just upstream of the regular sample point, and little or no consumption of DOC by in-stream processes.

Wetland catchments show that wetland areas are major sources of DOC and that DOC concentration drops more rapidly downstream in these catchments than in non-wetland catchments Catchments with high percentages of forest also show a similar pattern of DOC concentration decrease downstream. Decrease in DOC concentration downstream in forested catchments indicate that forested catchments should produce more DOC than non-forested catchments. The pattern holds for different discharges and therefore is not discharge dependent.

The conclusions from this part of the study are that stream DOC concentrations of non-wetland and wetland catchments respond differently to changes in discharge. The reasons why the catchments differ are related to the different physical characteristics of the catchments. The slopes of the wetland catchments are all shallower than the non-wetland catchments meaning that response time of changing discharge to increased precipitation was different Soils in wetland catchments are poorly drained while soils in non-wetland catchments are well-drained. Water in the poorly drained soil remains in contact longer with sources and storage areas of DOC than in well-drained soils. Water flow in the soil is conditioned partially by the slope of a catchment, plus soil characteristics and antecedent wetness conditions and the two types of catchments produce different DOC concentrations due to differences in slope and soil drainage, which is reflected in discharge.

Study of soils maps of the eight catchments reveal differences in soils between wetland and non-wetland catchments. Percentage wetland (swamp, muck, peat, beaver ponds), drainage characteristics, and slope are three factors associated with observed differences in DOC concentration:discharge relationships One reason for different relationships between wetland catchments may be the presence of ponds and sluggish water in two of the catchments that acted as filters for DOC.

Question 4

The fourth question dealt with determination of seasonal changes in DOC concentration of stream water. The purpose here was to establish whether there were seasonal patterns to DOC concentration in the catchments and to determine if the patterns were different for non-wetland and wetland catchments. It has been shown that the two types of catchments produce different amounts of DOC and that DOC concentration of streams fluctuates with discharge Seasonal patterns in DOC concentration are a function of climatic factors (precipitation, temperature, snow melt, etc) and length of growing season In the eight catchments the growing season was the same and the climate was slightly different (related to differences in elevation)

Differences in the pattern of DOC concentration confirm the differences between non-wetland catchments noted previously. There was a drought in the study area in June and July (during the growing season) and it is not known to what extent the dry weather may have influenced the normal seasonal pattern. In order to show whether there was a seasonal pattern a simple regression of DOC concentration against Julian date was run. Plots of the residuals from the regression against Julian date showed that there was a sine-wave shape (Grieve, 1984) in the data, which indicates a seasonal pattern, in Catchments 1, 2, and 4. Figures 19 and 20 show the sine-wave pattern for Catchment 4 and 1 (Catchment 2 is similar). The lack of a sine-wave shape in Catchment 3 is the same pattern seen in the wetland catchments which had higher DOC concentrations.

Wetland catchments responded differently than the non-wetland catchments. Lowest DOC concentrations were in early April and concentrations increased throughout spring until June when they decreased. Another increase occurred between July to late September-October, followed by a decrease for the rest of the study period. Catchment 8 showed very little fluctuation in DOC concentration while Catchment 5 showed a wide fluctuation in DOC concentration, but both maintained the same pattern as the other wetland catchments. There were no sine-wave shapes in the wetland catchments residual plots meaning that the was no seasonal pattern in five (4 wetland, 1 non-wetland) of the eight catchments. Figures 21 and 22 are typical of the pattern of residuals for the wetland catchments. The lack of a seasonal pattern means that there were factors other than season at work, which impart a pattern to the data

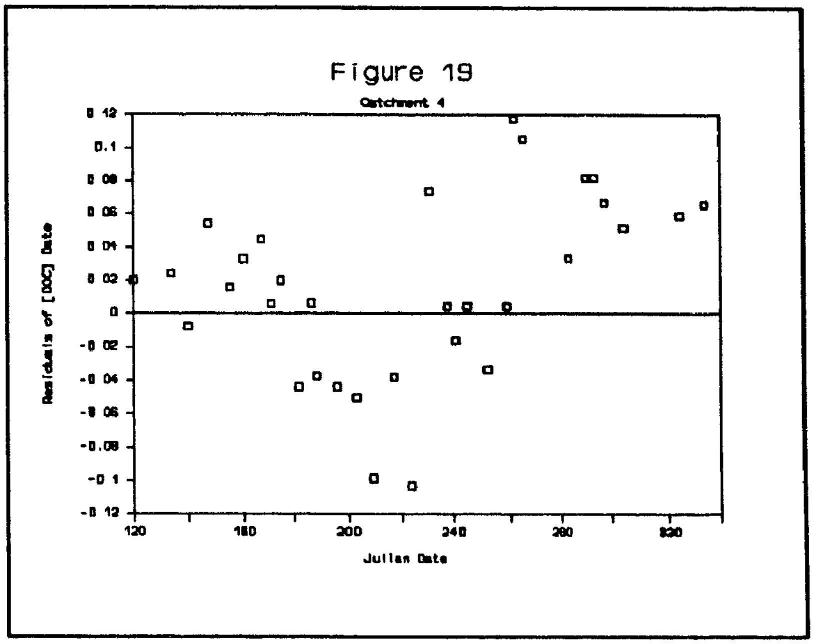


Figure 19
Catchment 4
Residuals of [DOC] Date
Julian Date

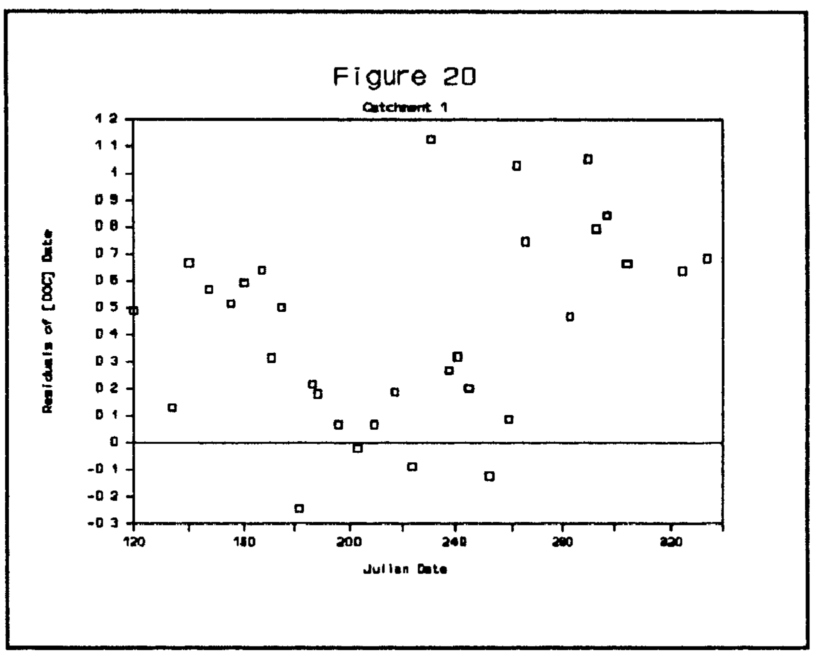


Figure 20
Catchment 1
Residuals of [DOC] Date
Julian Date

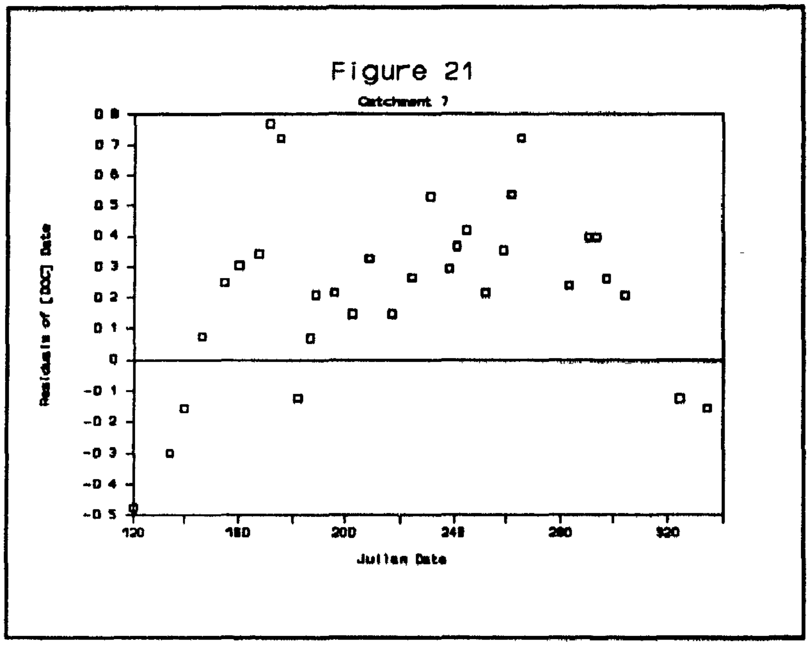


Figure 21

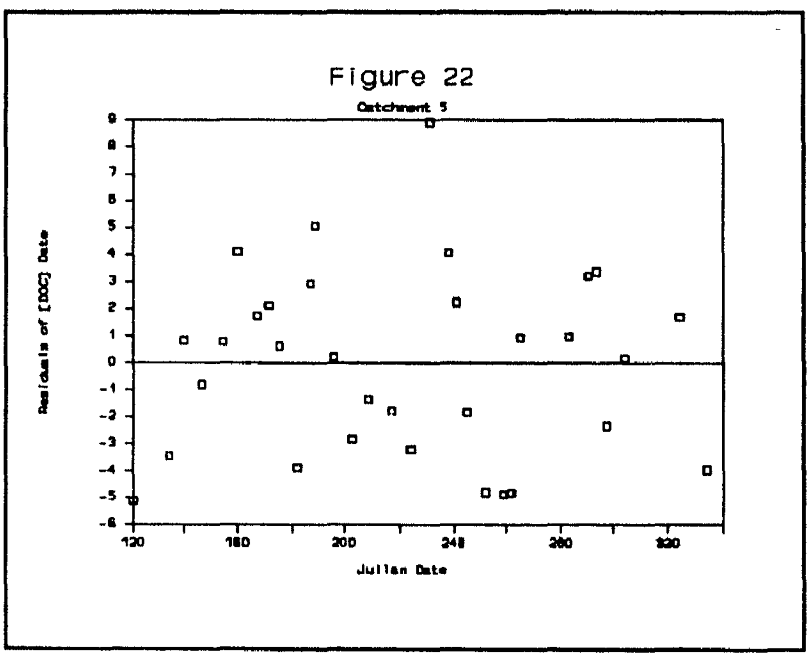


Figure 22

The conclusion from this question is that there are different patterns in DOC concentration between the two types of catchments and between the non-wetland catchments over the study period. Seasonal patterns were found in 3 of the non-wetland catchments, but not in the other 5 catchments. Differences in catchment physical characteristics and discharge were probably over-riding factors that obliterated any seasonal pattern (sine-wave pattern in the residuals) in 5 of the catchments. Adding the seasonal pattern data to the discharge:DOC relationships from above it can be seen that only three of the non-wetland catchments showed any significant relationships and these same catchments were the only ones with true seasonal patterns. The results from the other five catchments confirm different patterns between the catchments, but the patterns are too complex to ascribe them to season alone.

Question 5

The fifth question was concerned with establishing whether there were differences in DOC concentration between catchments of varying physical characteristics. Regression analysis techniques were utilized in order to create a predictive model of DOC concentration based on physical characteristics of the catchments. Results of question 5 are discussed separately in the following section on regression analysis.

REGRESSION ANALYSIS

The results from testing the model on the 8 main catchments are reported in this chapter while the results of the broader sampling of the 34 other catchments will be discussed in Chapter 4.

The Model

In order to create a predictive model for mean DOC concentration it was necessary to quantify the physical factors associated with the occurrence of DOC within the catchments. Once associations between physical factors and DOC occurrence were established, determination of which physical factor(s) were most responsible for variations in DOC concentration in stream water began. Multiple regression using a least squares fit (GLM procedure, SAS, 1982) was the method used to create the predictive equation of DOC concentration for stream water.

Variable Testing

The original set of variables included 5 physical characteristics, therefore multiple regression was employed. A test of normality (UNIVARIATE Procedure, SAS, 1982) shows the dependent variable was not normally distributed unless it was logged. The transformed dependent variable was normally distributed throughout the range of the independent variables (Neter et al., 1985). Scatter plots were made with ln (mean DOC concentration) as the dependent variable against the untransformed independent variables and only Percentage Wetland and Slope were linear with the dependent variable.

The design or data space (Draper and Smith, 1980) of the model variables revealed that several of the variables were correlated and formed linear relationships. Scatter plots of the chosen independent variables plotted against the dependent variable (to test whether the relationships were linear) and against each other (to see if there was any correlation in the independent variables) were made. The scatter plots were valuable for showing the form of functional relationship between the variables (Winkler and Hays, 1975; Sachs, 1984).

Scatter plots of the five independent variables on mean DOC concentration showed that Percentage Wetland and Slope form linear relationships, positive and negative respectively, with mean DOC concentration but Area, Percentage Forest, and Drainage do not, requiring a transformation.

Another diagnostic test was to plot ln (mean DOC concentration) against the natural log of the independent variables (Sachs, 1984). In the ln-ln transformation Percentage Wetland, Slope, and Drainage were linear and Percentage Forest, and Area were not. The ln-ln transformation maintained the linear nature of the data set that was necessary for further work involving linear regression analysis (Cook and Weisberg, 1982; Montgomery and Peck, 1982)

Testing the independent variables for normality and linearity through scatter plots and simple diagnostic tests led to the rejection of two of the five variables (Area, and Percent Forest) because they were not normally distributed and nonlinear with the dependent variable. One diagnostic test used to determine the strength of the variables for prediction was the RSQUARE procedure (SAS, 1982) which chooses the best r^2 value for a model by regressing each variable against the dependent variable. The model steps through the data to fit the best two variable model and so on until a model with n variables is created where n equals the number of variables in the data set. This form of model "fitting" allows the researcher to determine which variables are contributing the most to the variation in the dependent variable and which are not. Area and Percent Forest were found to add little to the explained variation in DOC concentration, so based on this and the fact that they were not linear with the dependent variable they were rejected from further consideration.

Correlation Matrix And Collinearity Diagnostics

In order to test for correlation and collinearity between the independent variables, a Pearson Correlation matrix (CORR Procedure, SAS, 1982) was created (APPENDIX B, Table 2). Large correlation coefficient (r) values indicate that variables vary together and may be collinear. Percentage Wetland, Slope, and Drainage were found to be highly correlated and collinear (APPENDIX B, Table 3) (REG procedure with COLLIN option, SAS, 1985), a fact previously indicated in their design space plots

The strength of the linear relationship between variables is shown by the magnitude of the correlation coefficient (r) (Sachs, 1984) High correlation, greater than 0 60, causes confusion about the predictive nature of the independent variables on the dependent variable. When independent variables are highly correlated with one another the model is biased and one or more of the variables can effectively be removed from the model (Winkler and Hays, 1975; Steel and Torrie, 1980; Morrison, 1980; Sachs, 1984). Because of the small sample size (n=8) collinearity was a problem in the data.

There was collinearity in the data set between ln Percentage Wetland, ln Drainage, and ln Slope. The assumption of the collinearity procedure is that if a variable has a high condition number (calculated as the square roots of the ratio of the largest eigenvalue to each individual eigenvalue (SAS, 1985)) and a high proportion of the variation on 2 or more variables then there is multicollinearity in the data set The presence of multicollinearity means that one or more variables must be rejected from the model to maintain statistical accuracy.

Model Results

The eight catchments were chosen because variations in catchment physical characteristics can be related to differences in DOC concentration between catchments. The predictive model works to provide the mean DOC concentration of a sample of stream water. The model is based on eight catchments, sampled 32 times over the study period, which provide eight values for the regression analysis

Residual Plots, Regression, and Adjusted Variable Plots

Based on the results of scatter plots, transformations of variables, and diagnostics, a general regression was run to get an indication of the relationship between the independent variables and the dependent variable. Based on t and F statistics from the regression ln Percentage Wetland, ln Slope, and ln Drainage were the independent variables used in the model equation

Plots of residuals can be used as simple tests of whether the regression is linear (Sachs, 1984). Six departures from the simple linear regression with normal errors that can be checked with residual plots are: 1) the regression function is not linear; 2) the error terms do not have constant variance; 3) the error terms are not independent; 4) an outlier may invalidate the model; 5) error terms are not normally distributed; and 6) there may be another independent variable omitted from the model (Neter et al., 1985)

Normality of error terms was checked by plotting the residuals against the expected value and marking off the standard deviations from the mean value (Neter et al., 1985). The normal distribution will follow a set pattern, that a) approximately 68.2% of the values will be within ± 1 0 standard deviation of the mean; b) 95 4% of the values fall within ± 2 0 standard deviations of the mean; and c) 99.7% fall within ± 3 0 standard deviations of the mean (Ebdon, 1977)

Independence of the error terms was checked by studying the way the residuals were scattered about the zero (mean) line (Neter et al., 1985) If the scatter of points around the line is random then the errors are independent If the residuals plot in a constant pattern (e.g. one is positive and the next is negative and then repeating this throughout, or if there is some linear pattern to the residuals) the assumption of independence is not valid Another test involved plotting the residuals regression against time. A random cloud of points results when errors are independent, if some linear pattern results then the errors are not independent and the model is not valid. In both cases the errors proved to be independent for the model.

Adjusted variable plots were made to check whether the omission of variables might have an effect on the regression model (Chambers et al., 1983; Weisberg, 1980). The adjusted variable plots were needed because of the multicollinearity in the data set. In adjusted variable plots residuals of regressing k - 1 independent variables against the dependent variable are plotted against residuals of the k^{th} independent variable regressed against the k - 1 independent variables. Adjusted plots show whether omitted variables account for a significant amount of the unexplained variation in the dependent variable (Chambers et al , 1983) All three independent variables (ln Percentage Wetland, ln Slope, and ln Drainage) accounted for some of the unexplained variation in the dependent variable. ln Percentage Wetland and ln Slope had strong linear patterns in the adjusted variable plots, but due to non linearity with ln DOC concentration they were not considered valid, although they appeared to account for a large amount of the unexplained variation in the dependent variable The reason for the linear patterns was the multicollinearity in the data set which may be masking the true effects of the variables.

The original design space plots and the Pearson Correlation matrix of independent variables reveal definite correlation which introduces bias to the model. The decision to remove variables was partially based on the fact that correlated data is collinear and variations in one cause variations in the other variable(s), which can effect the estimate of the predicted variable The other reason was that two of the variables did not form linear relationships with ln DOC concentration.

A model building routine (RSQUARE Procedure, SAS, 1982) was run to establish which variable accounted for the most variation in the dependent variable. The decision to include ln(Drainage) (r^2 = 0 890) instead of ln(Percentage Wetland) (r^2 = 0 853) and ln(Slope) (r^2 = 0 754) in the model was based on the fact that ln(Drainage) had equal variance and the other two did not. All results were significant at the 0.01 level of confidence

Conclusions On Regression

Residual plots from simple regressions of each independent variable on the dependent variable were studied to assess the normality and validity of each variable for inclusion in the model Three variables were included in a general model equation based on scatter plots. A residual plot of the regression for all three variables indicated that the variance was not constant or equal. The correlation matrix, collinearity diagnostics, model building procedure, and adjusted variable plots were all employed to ensure that the variables were the proper ones for the model It was determined that there was a high degree of multicollinearity in the data and that only one variable could be included in the final model equation

The final model for the original eight catchments was of the form·

$$\ln(\text{mean DOC}) = a + b_1 \ln(\text{drainage}) + E$$

The values of the estimates were:

$$a = 3.78$$

$$b_1 = -1.93$$

which gave the final regression equation:

$$\ln(\text{mean DOC}) = 3.78 - 1.93(\ln(\text{drainage})) + E$$

$$\text{Mean DOC} = e^{3.78} \times (\text{drainage})^{-1.93} + E$$

$r^2 = 0.89$ Standard Error = 0.28

$n = 8$ Level of Significance = 0.01.

The variance in the model was constant and the residuals were independent. The use of scatter plots to determine which variables were linear with the dependent variable pointed out two facts. First, a transformation of the data was necessary, and second, scatter plots alone cannot determine the adequacy of a variable and other diagnostic tests are necessary For larger data sets ln Percentage wetland and/or ln Slope may also be used as predictors, but for this data set they are not statistically correct.

The conclusion of question 5 is there is a predictive model which shows differences in mean DOC concentration between a range of catchments based on physical factors. The ln-ln model did not suffer from any of the six departures from simple linear regression Table 12 shows the observed mean DOC concentrations from the samples collected during the study and the predicted mean DOC concentrations obtained from the model. The model does generate values of mean DOC concentration that can be used to separate a data set of wetland and non-wetland catchments.

TABLE 12

Observed, Predicted and Residual Values
of DOC Concentration Obtained
From the Regression Model

Catchment	Observed	Predicted	Residual
1	1.353	1 104	0.249
2	1 256	1 659	-0.403
3	1.978	1.659	0.319
4	1.338	1.659	-0 321
5	2.671	2 995	-0 324
6	3.468	2.996	0 472
7	3.090	2.995	0.095
8	3.690	3.778	-0 088

Note: All values are natural logs, all results are significant at 99% level of confidence.

WATER CHEMISTRY ANALYSES

Concentrations of DOC are dependent on physical characteristics of catchments, but also on chemical properties of water. All stream samples were analyzed for Electrical Conductivity (Ec) and pH and selected samples were analyzed for cations and anions to provide a broad chemical picture of stream water. APPENDIX C (Table 1) shows the Ec, pH, and cations and anions with DOC. Table 13 lists the mean DOC, mean Ec and mean pH for the eight catchments. Simple regressions were run on the Ec against the cations and anions to see if Ec could be used as a quick method for estimating ionic concentration in stream water.

Wetland catchments had lower Ec values than non-wetland catchments with the exception of Catchment 4. Cation analysis determined that Ca^{++} was the dominant cation in all eight catchments Mg^{+} was the second most dominant cation followed by Na^{+}, K^{+}, and total iron (Fe*). For instance, three of the wetland catchments (5,7,8) had higher Fe*

TABLE 13

Mean DOC, Mean Ec, and Mean pH
for the Eight Catchments

Catchment #	DOC	Ec	pH
1	3.9	131	7.1
2	3.5	153	7.1
3	7.2	91	6.7
4	3.8	70	6.8
5 *	14.5	78	6.5
6 *	32.1	48	6.3
7 *	21.9	40	6.3
8 *	40.0	36	5.9

Note: All values are means for 32 sample dates for the 8 catchments; *=wetland catchments, DOC is in mg/l; Ec is in uS/cm.

than K^+ values and the other (6) had higher Na^+ than Mg^+ values Ca^{++} and Mg^+ buffer the pH above 6 7 for non-wetland catchments (where DOC concentration is low) and the higher DOC concentrations in wetlands buffer the pH below 6 5.

Wetland streams have lower mean pH than non-wetland streams, which may be a function of the higher DOC concentration in water flowing out of wetland areas The pH data show average pH of wetland catchment streams was lower than pH of non-wetland streams Low pH values were associated with high DOC concentrations due to DOC buffering pH in wetland catchments Cations (mainly Ca and Mg) buffered pH in non-wetland catchments. Wetland stream average pH ranged from 5 9 to 6 5 and non-wetland stream average pH ranged from 6 7 to 7 1 The lowest pH values occurred from early September to mid October The non-wetland catchments tended to have higher pH values during June, July, and August. The wetland catchments did not follow a set pattern of highest pH values, but showed more fluctuation throughout the study period

Anion analysis determined that SO_4^{--} was the dominant anion in 3 of the wetland catchments and CO_3^{--} was the dominant anion in the other 5 catchments. Wetland catchments have lower anion concentrations than non-wetland catchments. Catchment 6 exhibits lower NO_3^- concentration than the other catchments. Low NO_3^- levels may be due to nitrogen uptake by benthic organisms in the beaver ponds found along the course of the stream Catchment 4 is a non-wetland catchment that exhibits Cl^- and NO_3^- concentrations similar to wetland catchments, but the SO_4^{--} concentrations are similar to the other non-wetland catchments. The possible explanation is that farming is no longer actively pursued in Catchment 4.

Low levels of cations in stream water of four out of eight catchments may be related to: a) lack of fertilizer input to the catchment, b) percentage forest land in the catchment, c) percentage wetland in the catchment and/or d) soil characteristics. Parent material for soils includes schist, slate, and sandstone which provide high levels of Ca^{++}, Mg^+, and Na^+ Fertilizer application causes high levels of K^+ in certain catchments. Concentration of Fe* were highest in the wetland catchments.

Table 14 lists the regression equations for Ec against each cation and anion The low r^2 values for Na^+, Fe^*, and Cl^- are due to nonlinear spread of the data (APPENDIX C, Figs. 1-8). The data do show that Ec can be used as an indicator of cation and anion concentration (e.g. high Ec means high concentration of cations and/or anions). Wetland catchment streams tend to have lower ionic concentrations than non-wetland streams. The non-wetland streams have higher concentrations of Ca^{++} and Mg^{+} that buffer the pH upward (more alkaline), while wetland streams have higher DOC (and lower ionic concentrations of Ca^{++} and Mg^{+}) that buffers pH downward. As with the spectrophotometric (absorbance) method (p. 29) of DOC estimation, Ec is a good surrogate for quickly estimating ionic concentrations in stream water.

Table 14
Relationships Between Cations, Anions, and
Electrical Conductivity

Ion	Equation	r^2	S.E.	Sig. Level
Ca^{++}	Y = 0.58 + 0.15(X)	0.79	0.021	0.0001
Mg^{+}	Y = 15.44 + 0.28(X)	0.88	0.030	0.0001
K^{+}	Y = 19.27 + 2.34(X)	0.72	0.392	0.0001
Na^{+}	Y = 25.08 + 0.40(X)	0.23	0.200	0.0628
Fe*	Y = 79.14 - 2.87(X)	0.41	0.920	0.0077
Cl^{-}	Y = 18.65 + 0.35(X)	0.52	0.090	0.0017
SO_4^{--}	Y = -59.49 + 0.65(X)	0.72	0.110	0.0001
NO_3^{-}	Y = 32.853 + 1.20(X)	0.82	0.150	0.0001
CO_3^{--}	Y = 28.40 + 0.09(X)	0.92	0.007	0.0001

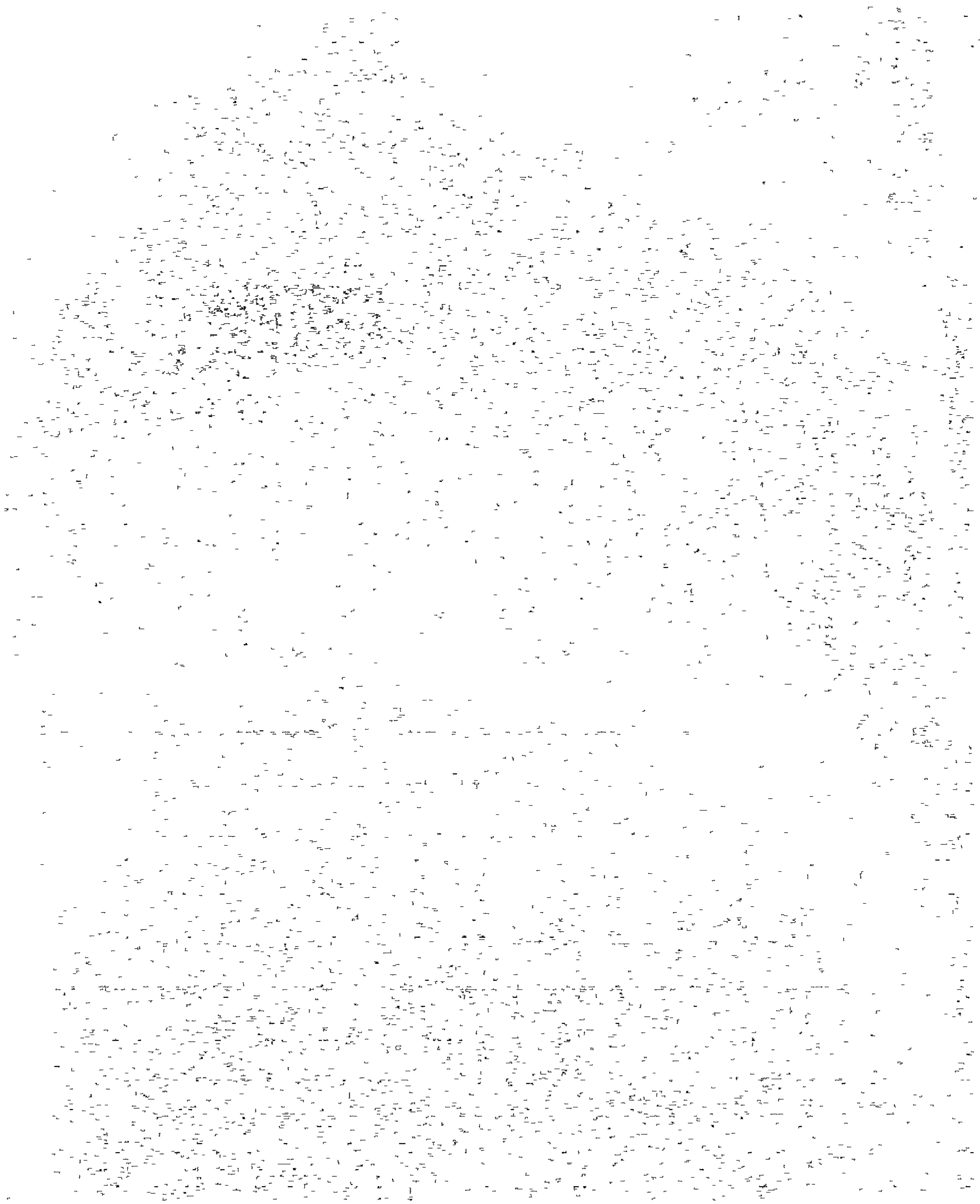
Note: Y=Electrical conductivity; X=concentration of ion in ueq/l;
Fe* represents total iron (Fe^{+2} and Fe^{+3}).

CONCLUSION

The five questions proposed in Chapter 1 have been answered for the 8 catchments leading to several conclusions. First, there are significant differences in mean DOC concentration between wetland and non-wetland catchments. Second, percentage forest is not a good indicator of DOC concentration for non-wetland (or even wetland) catchments. Third, there are different responses of DOC to discharge for wetland catchments, but non-wetland catchments show a positive relationship. The reason for the different responses is related to the drainage or hydrologic pathways within the catchments Four, there are different seasonal patterns to DOC concentration between the two types of catchments. Five, there are differences in mean DOC concentration between catchments that can be predicted by soil drainage class (i.e. hydrologic pathways).

Ec, pH, and cation and anion concentrations can be used to differentiate between types of catchments. Wetland catchments tend to have higher DOC, lower pH, lower cation concentration, and lower anion concentration than non-wetland catchments. The exception to the wetland pattern changes when farming or some other form of disturbance changes the surface layers of the soil in the catchment, which can increase chemical weathering. Non-wetland catchments tend to have lower DOC, higher pH, higher cations and anion concentrations than the wetland catchments.

Slope and soil characteristics play a role in the weathering process Steep slopes and permeable soils allow water to percolate downward and through the soil system quickly. The steeper sloped and better drained catchments have higher ionic concentrations in stream water than the lower sloped and poorer drained catchments Wetland Catchment 5 reacts differently than the other three wetland catchments because its slope is greater Farming is also active on Catchment 5 which opens more soil to chemical weathering Of the non-wetland catchments, number 4 has a different pattern of ionic concentrations than the other three. There was no active farming on Catchment 4, so the soil was not as exposed to chemical weathering as the other three catchments.



CHAPTER 4

INTRODUCTION

The next phase of the study concerned testing the model's predictive ability of DOC concentration from simple catchment characteristics to a wider range of catchments. The data set contained 42 catchments sampled four times from August to November.

The 42 catchments (Table 6, p. 21) are from two physiographic regions, 17 catchments are in the St. Lawrence Lowland south of Montreal and 25 are in the Appalachian Upland east of Montreal. The original 8 catchments are included in the Upland group. The two regions provide a wider range of slope, drainage, and percentage wetland than was encountered in the original eight catchments.

The Appalachian Uplands are hilly to mountainous and slopes range from 8.4% to 49.5%. The drainage in the Uplands ranges from poor (1.0) to excellent (4.5). Percentage wetland varies from 0 to 69% with the majority of catchments having less than 20% wetland area. Streams in the Upland (with several exceptions) are fast moving and have rocky beds where mixing is uniform.

The St. Lawrence Lowlands are very flat and slopes range from 1.1% to 12.5%. Drainage ranges from very poor (0.0) to good (3.8). Percentage wetland ranged from 0.0 to 79.0% with the majority of catchments having greater than 20% wetland area. Streams in the Lowland are generally slow moving and lack the rocky beds found in Upland streams.

In order to test whether the model from Chapter 3 of ln(DOC concentration) = ln(Drainage) was useful in a wider range of catchments it was run with the data on the 42 catchments. Table 15 shows the data from the simple regression. The data show that the model accounts for 21 to 37% of the variation in DOC.

TABLE 15

Regression For The Sample Data
On All 42 Catchments

Date	Equation	r^2	S.E.	Sig. Level
August	Y = 2.85 - 0.88(X)	0.22	0.24	0.004
September	Y = 2.86 - 0.73(X)	0.21	0.19	0.003
October	Y = 2.85 - 0.66(X)	0.22	0.14	0.017
November	Y = 2.96 - 0.87(X)	0.37	0.17	0.001

Note: Y=ln(DOC concentration); X=ln(Drainage).

The assumptions of the model that were satisfied with the smaller data set are not valid for the simple (ln DOC-ln Drainage) model with the larger data set. The addition of catchments with more variety in physical characteristics causes the model to lose some of its predictive ability. Although the results are significant, the data indicate that a multiple regression should be set up to account for more of the variation in the DOC concentration. The following discussion deals with two approaches to a solution of the modelling problem.

REGRESSION RESULTS

The above section shows that the simple model fails to account for much of the variation in the dependent variable. To remedy this, a multiple regression equation was set up using the same variables from Chapter 2 as the predictors and DOC concentration as the dependent variable. DOC concentration was normalized by taking the natural log of the values. The model, ln(DOC concentration) = Drainage + Slope + Percentage Wetland + Percentage Forest + Area, was used to test the hypothesis that there were differences in DOC concentration between catchments of varying physical characteristics. In order to facilitate testing, the data were divided by sample date. Preliminary tests (PROC RSQUARE, SAS, 1982) found that Area and Percentage Forest, combined, accounted for mo more than 1% of the variation in DOC concentration and were dropped from further consideration. Table 16 shows the results of regression for the four sample dates

TABLE 16

Regression For The Four Sample Dates
On All 42 Catchments

Date	Equation	r^2	Stan. Error	Sig. Level
August	$Y = 2.64 - 0.13(X_1)$	0.02		
	$+ 0.01(X_2)$	0.30		
	$- 0.02(X_3)$	0.05		
	Total:	0.37	0.47	0.0012
September	$Y = 2.61 - 0.20(X_1)$	0.05		
	$+ 0.01(X_2)$	0.26		
	$- 0.00(X_3)$	0.00		
	Total.	0 32	0.39	0.0021
October	$Y = 1.91 + 0.03(X_1)$	0.00		
	$+ 0.02(X_2)$	0.33		
	$- 0\ 00(X_3)$	0.00		
	Total:	0.33	0.45	0.0018
November	$Y = 2.37 - 0.05(X_1)$	0.00		
	$+ 0.02(X_2)$	0.67		
	$- 0.01(X_3)$	0.06		
	Total:	0.73	0.24	0.0001

Note: Y=ln(DOC concentration), X_1=Drainage, X_2=Percentage Wetland, X_3=Slope

The model results were all significant ($p < 0.01$) and the standard errors of the estimate were all low (0 24 to 0 47) The variance in the residuals was constant, the error terms were normally distributed and independent, and the regression function was linear Using easily obtainable data from maps and aerial photographs a quick assessment of a catchments potential for DOC concentration can be established with the model. A stepwise regression (PROC STEPWISE, SAS, 1985) was used to evaluate each variables contribution to the variation in DOC.

The presence of slight collinearity (APPENDIX D) within the data set was probably the reason for the low r^2 values for Drainage and Slope. Percentage Wetland accounted for the majority (26 to 67%) of the variation in DOC concentration Percentage Wetland was positively related to ln(DOC concentration) and catchments with wetland areas had higher concentrations of DOC Slope and Drainage varied together (collinear) and were negatively related to ln(DOC concentration), except in October Collinearity between Drainage and Slope causes the results to be biased and together they accounted for between 0 0 to 7% of the variation in DOC concentration

The differences in the DOC concentration, as predicted by the model, were more pronounced in November than in any of the other months. The reasons why November had a stronger predictive ability may be due to seasonal climatic factors, such as changing temperature that causes water on the ground surface to freeze blocking infiltration, increased precipitation and higher discharge, and lack of organic matter input from live plants and/or leaf fall The seasonal factors may be overriding the physical characteristics by changing the pathways, sources, sinks, and storage areas of DOC within the catchments

Table 17

Precipitation Data
1988
Bonsecours, Quebec
45° 24′ N 72° 16′ W

Day	April	May	June	July	Aug.	Sept.	Oct.	Nov.
1	0.0	0.0	0.0	11.4	0.0	0.0	0.0	49.2
2	0.0	0.0	0.0	2.6	0.0	0.0	21.0	5.8
3	2.6	0.0	0.0	0.0	23.4	0.0	0.0	0.0
4	5.2	0.0	0 0	0.0	0 0	6.6	0.0	0.0
5	0.0	0.0	1.0	0.0	12.8	4.0	8.4	8.4
6	0.0	0 0	0 0	0.0	6 0	0 0	0.8	2.4
7	0 0	0 0	0 0	1.4	7 0	0.0	0.0	10.4
8	0.0	0 0	0.0	0.0	0.0	0 0	2 2	10.4
9	0.0	0 0	1 6	0.0	3.0	0 0	7.0	0.0
10	1.4	0.0	1 4	0 0	0.0	0 0	3.6	0.0
11	0.0	1 4	0 0	3.4	0 0	0.0	3.4	0 0
12	0.0	0.0	0.0	6.0	6 2	5.8	1.6	0.0
13	0 0	11 8	0 0	2 4	11.6	10.6	0 0	12.0
14	1.4	0 0	0 0	12.4	81.6	7 2	2 2	2.0
15	5 8	0 0	0 2	2.2	19 8	0 0	0.0	0.0
16	2.2	22 0	0 0	1.2	1.6	0 0	0 0	5 4
17	8.2	0 0	0 0	0 4	1 4	25 2	0.0	3.0
18	4 2	0 0	0 0	1 4	0 0	0 8	3.6	0.0
19	0.0	0.0	0 0	6.6	0.0	0 0	0.0	0.0
20	0.0	0 0	7 8	0.0	3 6	18.2	0.0	11 8
21	2.0	0 0	0 0	1 4	1 4	1 0	6.0	3.0
22	7.4	0 0	19 2	0 0	0.0	0 0	4 2	0.0
23	9.4	2 6	0 0	0 0	0.0	4.2	0.4	0 0
24	9 6	0 0	0 4	4.0	5.6	0.0	1 8	0.0
25	0 0	7 6	25 6	6.0	1.4	0.0	1 0	0 0
26	4 0	5 2	2 0	5 0	0 0	0.0	0.0	14 6
27	0 0	0 0	0 0	0.0	2.4	0 0	0.0	4.2
28	3 4	0.0	6 8	0.0	17 2	0.0	7 2	6 0
29	0.0	3.6	0 0	0.0	5.0	0.0	0.0	0.0
30	3.6	0.0	23 4	3.4	0.0	0.0	0.0	0 0
31		0 0		0.0	0.0		0.0	
Monthly Totals:	70 4	54.2	82.2	71.2	211.0	83 6	74.4	148.4
30 Year Mean:	74 1	65.6	82.2	90.0	91.9	88.4	75.5	81.0

Note· All values in mm.

Precipitation data in Table 17 shows that the monthly average of November was higher than October and September and coupled with the facts that harvest was over and deciduous forested areas were mostly devoid of leaves, any precipitation falling would avoid interception by leaves on trees. The lack of interception in the deciduous forested areas means that precipitation has a shorter and quicker route to the ground and to the stream. Areas with evergreen species could still receive inputs of DOC from leave drip. Several frosts had occurred in November prior to sampling and ice was present in several streams which would indicate that the surface and subsurface pathways in the soil could have been modified. Precipitation falling on the frozen surface of the ground as rain, would flow overland and not infiltrate meaning quicker response of discharge to storm events.

As noted above, wetland and non-wetland catchments respond differently to storm events and the differences may be heightened in late fall when the non-wetland catchments are devoid of one of their terrestrial vegetative DOC sources (i.e living tree leaves), while the wetland catchments still have bogs, swamps, and organic soils to supply DOC. This fact, coupled with the changes in climatic factors, would justify the difference in the predictive ability of the model for November.

The differences in physical characteristics between the catchments can be used to predict DOC concentration, but seasonal changes affecting sources, sinks, storage areas, and pathways must also be considered. Non-wetland catchments tend to show a seasonal pattern to DOC concentration while wetland catchments are more confusing. The seasonal effect (large in non-wetland catchments) may be another reason why the November data show better prediction of DOC concentration (i.e. there is a sharp difference between the two types of catchment).

VARIATIONS IN DOC CONCENTRATION BETWEEN REGIONS

It was found that there were differences in the overall physical characteristics between the Upland and Lowland catchments. In order to test whether there were differences in DOC concentrations between the two regions, multiple regression was employed on two sets of data from the 42 catchments Table 6 (p. 21) shows the break down of catchments, 25 Upland and 17 Lowland. Two questions were tested with the new data a) was there a difference in the model's predictive ability based on region, and b) was there a seasonal pattern in the data.

Differences in DOC concentration between the two regions were seen in the different DOC concentrations of streams in the regions The main differences between catchments in the two regions were drainage and slope Drainage was generally poorer in the Lowland due to the low slope. Although not the main focus of the study, regional differences between catchments of similar size and land use were investigated Table 18 shows the average (of four sample dates) DOC concentration for the two regions

TABLE 18

DOC By Region

Region	DOC concentration
Upland	11.6 mg/l
Lowland	19 4 mg/l

In order to test whether there were differences in the model's predictive ability between regions the data were divided into

Lowland and Upland catchments by sample date Table 19 shows the results of running multiple regression on the two data sets The data show that there was a difference in the ln(DOC concentration) between catchments in the two regions The model tends to produce more significant results in the Upland catchments, except for November. As seen in Table 18, the November data were anomalous for the whole data set, so too were the data for November when broken down into region by date The model's predictive ability changed over the study period and it is not known whether this is due to season, physical characteristics of the catchments, or both in conjunction

The sign of each coefficient (X), in Table 19, shows the relationship of the variable to ln(DOC concentration). For the Lowland group the Drainage variable carried a negative sign meaning that it was inversely related to DOC concentration Percentage Wetland initially carried a negative sign (August), but it accounted for none of the variation in DOC at that time The sign was positive for the other sample dates (September - November) meaning that DOC concentration increased with increasing percentage wetland Percentage wetland accounted for more and more of the explained variation in ln(DOC concentration) over the study period The sign of the Slope coefficient was both positive and negative The negative sign occurred where Slope accounted for < 0.1% of the variation in DOC concentration The reason for the positive sign may lie in the fact that slopes are very low in the region and that slight changes in slope may alter the pathways of DOC enough to cause differences in the DOC concentration in streams Contrary to the discussion on slope in Chapter 1, DOC concentrations increased with increasing slope in the Lowland in August and October

TABLE 19

DOC Concentration For Four Sample Dates
By Physiographic Region

Region	Date	Equation	r^2	S.E.	Sig. Level
Lowland	August 4/8	Y = 2.72 - 0.29(X_1)	0.05		
		- 0.00(X_2)	0.00		
		+ 0.08(X_3)	0.08		
		Totals:	0.13	0.75	0.4072
	September 21/9	Y = 2.57 - 0.22(X_1)	0.21		
		+ 0.01(X_2)	0.03		
		- 0.01(X_3)	0.00		
		Totals:	0.24	0.67	0.1822
	October 19/10	Y = 1.71 - 0.13(X_1)	0.01		
		+ 0.02(X_2)	0.21		
		+ 0.09(X_3)	0 04		
		Totals:	0.26	0.82	0.4153
	November 30/11	Y = 2.22 - 0.07(X_1)	0.01		
		+ 0.02(X_2)	0.59		
		- 0.00(X_3)	0.00		
		Totals:	0.60	0.38	0.0041
Upland	August 4/8	Y = 2.66 - 0 09(X_1)	0.01		
		+ 0.02(X_2)	0 52		
		- 0 02(X_3)	0.07		
		Totals:	0 60	0.63	0.0002
	September 21/9	Y = 2.88 - 0.11(X_1)	0.01		
		+ 0.02(X_2)	0.54		
		- 0.17(X_3)	0 08		
		Totals:	0.67	0.43	0.0001
	October 19/10	Y = 2.38 + 0.05(X_1)	0.00		
		+ 0.03(X_2)	0 57		
		- 0.02(X_3)	0 05		
		Totals:	0.62	0.47	0.0001
	November 30/11	Y = 1.57 + 0.11(X_1)	0.02		
		+ 0.03(X_2)	0.31		
		+ 0.00(X_3)	0.00		
		Totals:	0.33	0.59	0.0350

Note: Y=ln(DOC concentration); X_1=Drainage, X_2=Percentage Wetland, X_3=Slope.

In the Upland region Percentage Wetland was positively related to ln(DOC concentration) Percentage Wetland accounted for 31 to 57% of the variation in ln(DOC concentration). Drainage was at first negatively related to ln(DOC concentration), then positively related Drainage never accounted for more than 2% of the variation in ln(DOC concentration) Slope was negatively related to ln(DOC concentration) except in November when it accounted for < 0 01% of the variation

The model's overall predictive ability decreased in November for the Upland region which may be associated with climatic factors The Upland area experienced several frosts which may have caused alterations to the surface of wetland areas. Standing water and saturated ground at the surface may have frozen, changing the surface and shallow subsurface pathways of DOC in the wetland catchments Changes in sources, sinks, and storage areas of DOC were also altered due to seasonal variations in climate.

In order to check whether precipitation had an effect on the DOC concentration that may have caused the pattern in r^2 values in Table 18, data from Table 17 was used to get an estimate of the rainfall one week prior to sampling on the four dates. The precipitation prior to the four dates are as follows·

July 28 - August 4	26.8 mm
September 14 - September 21	52.4 mm
October 12 - October 19	7.4 mm
November 23 - November 30	24 8 mm

The precipitation data show that the model's changing predictive ability for the November data was probably not due to precipitation alone In the Upland catchments the statistical results for August, September and October are similar in r^2, S.E., and significance, but the precipitation data were quite variable. Based on the precipitation data alone, it would appear that November should have followed the same pattern as the other three sample dates, producing a higher r^2 value. The Lowland data show a similar anomaly in the results, whereby November has much higher r^2, lower S.E., and is significant at $p<0.0041$. The precipitation data indicate that the Lowland statistical results for November should have fallen between October and August, but they did not.

Seasonal change in climatic factors (including precipitation) was probably the reason why the data did not follow a set pattern for the whole study period August and September were still in the growing season and the statistical results for those dates were similar (as were the precipitation amounts). Autumn was well under way by the October sample date and the precipitation was low prior to sampling, but the results were similar to August and September. By mid November colder weather had set in and snowfall was recorded on the 2nd, 20th, and 28th. Although precipitation was low prior to the November sample, some factor other than physical characteristic was responsible for the changing predictive ability of the model. This points out that even though the physical characteristics of catchments may be different and cause differences in DOC concentration, seasonal variations in climate can also effect the DOC concentration.

It was shown in Chapter 3 that three of the four non-wetlands had distinct seasonal patterns in residual data from discharge versus date. Seasonal pattern (appearance of a sine-wave shape in residuals) can be used as a separator between catchments The multiple regression model also shows the effects of seasonal factors on the data set. The sample dates of August, September, and October are all similar in statistical results (by region) and all were dealt with before the season changed dramatically By the November sample date winter-like conditions had begun and this was shown in the statistical results by the r^2 values and SE values.

There are several reasons why the model produces different results for the Upland and Lowland regions. The Lowland region is more intensively farmed than the Upland and many of the wetland areas have been turned into fields for crops Farmers in the Lowland have cut ditches in wetlands to lower water tables, changing the hydrologic pathways of the wetlands Unfortunately, the only soil data for the Lowland was from 1944 and 1950 and the extent to which identified wetlands (from old maps and reports) have changed is not fully known The modification or disturbance of the natural drainage and hydrologic pathways in the Lowland caused the model results to be biased The Upland region has remained fairly stabilized, in terms of land use, for the past 20-30 years, so human disturbance or modification of hydrologic pathways does not affect the model's predictive ability in the region

Differences in the model's predictive ability may also be related to the varying physical characteristics of the catchments There was a wider range of wetland types in the Upland region Beaver ponds and swamps form the majority of the wetland areas in the Upland catchments while only four of the catchments have bogs present. In the Lowland the majority of wetland area is swamp or former bog. The low slope and poorly drained soils of the Lowland are indicative of swampy land. The Upland catchment's wetland areas are indicative of a more diverse and dynamic landscape than the Lowland. The data may also reflect differences in the way catchments in the two regions reacted to the drought conditions. Soils dry out more during drought conditions than they would under normal conditions, changing the flow of water in the soil (i.e. hydrologic pathways change).

By using physical characteristics of the catchments which are influenced by seasonal changes, some confusion arises from trying to determine whether the effect on stream DOC concentration is entirely physical, entirely seasonal, or a combination of the two. The effect that caused the November results shown in Table 18, is related to seasonal changes in climatic factors, which in turn, caused changes in the sources, sinks, storage areas, and pathways of DOC in the catchments.

WATER CHEMISTRY ANALYSES

The geochemistry of streams in the two regions differed as shown by the Ec and pH values in Table 20. The differences in Ec between the two regions is a factor of the different soils in the regions. In the Upland, soils tend be be derived from fluvioglacial processes and metamorphic parent material. Soils in the Lowland are associated with Champlain Sea deposits (sedimentary) and outwash from the Upland areas. Lowland soils contain more clay and water samples in the lab tended to produce chloride precipitates during digestion. From Table 20 it can be concluded that the geochemistry of the two regions is quite different and this may affect the predictive ability of the model. There may be some physical characteristic common to Lowland catchments that would account for the unexplained variation in DOC concentration.

TABLE 20

Average DOC, Ec, and pH For The 42 Catchments

Catchment Number	DOC (mg/l)	Ec (uS/cm)	pH
Upland Catchments			
1	3.9	131	7.1
2	3.5	153	7.1
3	7.2	91	6.7
4	3.8	70	6.8
5	14.5	78	6.5
6	32.1	48	6.3
7	21.9	40	6.3
8	40.0	36	5.9
9	10.2	51	6.4
10	3.0	79	6.9
11	7.5	126	6.8
12	5.9	37	6.6
13	3.9	160	7.1
14	9.0	152	6.7
15	3.4	58	6.9
16	14.0	229	6.5
17	7.9	58	6.3
18	9.4	88	6.7
19	29.6	202	6.8
20	7.2	71	6.6
21	17.2	320	6.7
22	22.1	48	6.2
23	11.6	113	6.9
24	24.4	93	6.4
25	11.2	78	6.9
Lowland Catchments			
26	7.7	598	7.3
27	15.2	375	6.9
28	14.2	554	7.2
29	4.4	415	7.2
30	16.5	510	6.9
31	40.1	453	7.0
32	8.2	390	6.8
33	16.1	324	6.8
34	39.5	327	6.6
35	7.4	460	7.5
36	11.1	488	7.4
37	25.3	536	7.3
38	11.6	519	7.0
39	10.1	355	6.9
40	18.2	606	7.2
41	29.7	526	7.2
42	29.4	167	6.4

The pH of the Lowland catchments is generally higher than the Upland catchments, which is a function of the different geochemistry of the stream water and different soils in the two regions. Even though there may be wetlands producing large amounts of acidic water (DOC-rich), the buffering effect of ions in soils keeps the pH higher in the Lowland than would be the case in the Upland where concentrations of ions are lower.

CONCLUSION

Percentage Wetland accounts for the majority of the variation in ln(DOC concentration) in the 42 catchments. The area of a catchment covered by wetland can be easily obtained from soils maps and aerial photographs allowing for a quick check of a catchment's DOC concentration A natural log transformation of DOC concentration was necessary for adherence to the regression rules of linearity, independence and constancy of error terms, and normality No such transformation was needed for the independent variables. Regression analysis showed that Percentage Wetland accounted for between 26 and 67% of the variation in ln(DOC concentration) over the four sample dates.

Water chemistry analyses pointed out that there were differences in stream water chemistry between the two regions Different soils and parent material were responsible for the different ionic concentrations (indicated by the Ec values) of streams in the two regions Laboratory findings of precipitates of chloride in many of the Lowland samples and none of the Upland samples reenforced the idea that stream water chemistry varied between regions. To what extent the difference in slope between the two regions affected the stream water chemistry is not known at this time.

CHAPTER 5

CONCLUSION

The above review and discussion have determined that there are differences in the DOC concentration between catchments based on physical characteristics of the catchments. The differences in physical characteristics are manifested in different drainage patterns, slopes, and percentage wetlands in the catchments. Differences in the DOC concentration between catchments are also associated with varying geochemical components of stream water, such as electrical conductivity, pH, and cation and anion concentrations.

Statistical methods showed that there was a significant difference in the DOC concentration of catchments with different percentages of wetland, slope and drainage patterns. Multicollinearity in the data and lack of linear relationships between ln (DOC concentration) and all but one variable led to a final model for the eight original catchments including only ln(Drainage). The interrelationships (collinearity) between drainage, slope and percentage wetland are important because soil characteristics tend to be the main control on water movement through a catchment. The hydrologic pathways of water, within a catchment, are functions of slope and soil drainage capability (i.e. permeability). The presence of wetland in a catchment is also a function of slope and drainage capability.

The model (ln(DOC concentration) = ln(Drainage) provides significant results based on the original data set, but not with the extended (42 catchment) data set. One problem was with old soils data (circa 1947, 1950) on which the Drainage variable was based. A multiple regression equation was formulated to handle the extended data set. The multiple regression model was ln(DOC concentration) = Drainage + Percentage Wetland + Slope and explained between 33 and 71% of the variation in DOC concentration. The 42 catchment data set was divided into two groups: a) by date, and b) by region and date.

The predictive ability of the model was different by date indicating a possible seasonal pattern to DOC concentration. A seasonal pattern was established in the original data set, which was a part of the extended data set, and the regression results confirmed it in the extended data set. Seasonal change was not the only factor in the models varying predictive ability. Seasonal changes tend to cause changes in the sources, sinks, storage areas, and pathways of DOC within a catchment so that it is difficult to separate seasonal influence from physical characteristics.

Regional differences between the St. Lawrence Lowland and the Appalachian Upland were established from the second grouping of data. The models predictive ability was different for the two groups. The values were more significant (although there was multicollinearity in the data) in the Upland than the Lowland, except for November The Upland catchments were more varied in physical characteristics which seemed to help in predicting DOC concentration. However, in November the model was not able to account for more than 25% of the variation in DOC concentration. The Lowland data showed the opposite trend, whereby, the model was unable to account for more than 30% of the variation in DOC concentration in August, September, and October.

One reason why the model showed different predicti·e abilities in the Lowland region was due to the amount of disturbance, farming activity, to the catchments. Disturbance has been seen (Meyer and Tate, 1983) to change the response of some catchments, but not all (Meyer et al., 1981) to precipitation events This change is a result of changing hydrologic pathways, sources, sinks and storage areas within the catchments. Changing the hydrologic pathways of former wetland areas also allows precipitation to percolate deeper into the soil and DOC to be more readily adsorbed. Removal of top layers of peat in former wetlands reduces the input of organic material to the soil. Cutting drainage ditches in former wetlands lowers the water table and reduces the saturated area of a catchment and improves the waters ability to infiltrate and percolate deeper into the soil. All of this leads to lower DOC concentration in streams flowing out of former wetlands, which comprised a large percentage of the catchments in the Lowland region that were used in this study. More recent data on soil and drainage conditions may help improve the predictive ability of the model in the Lowland region.

Seasonality of DOC concentration was conclusive in only three non-wetland catchments in the original eight catchments Wetland catchments experienced a spring low and rapid rise through the growing season and a decline in late fall. Non-wetland catchments DOC concentrations remained constant through spring and fluctuated in summer and declined in early fall. Electrical conductivity and pH followed definite patterns for non-wetland catchments and a more random pattern for wetland catchments, implying different responses for the two types of catchments.

Seasonal patterns of DOC concentration are a function of climatic factors which affect: the growing season of plants (sources), ground cover (sources and storage areas), soil temperature (freeze-thaw alters pathways), water temperature (biologic sources), precipitation input (sources and pathways), farming activity (sources and pathways), floods (sources, storage areas and pathways), and discharge (sources and storage areas). Lack of precipitation during the summer (June, July and September) drought caused the usual hydrologic pathways to be altered. In November, as winter approached, climatic factors began altering the hydrologic pathways creating different conditions in the stream water.

Based on the evidence from the above study which shows that wetland and non-wetland catchment differ significantly in DOC concentration because of different physical characteristics of the catchments, it was shown that soil drainage, percentage wetland, and slope provide the best means of predicting mean (annual) DOC concentration in stream water, at the small catchment level Although correlated these three characteristics can be used in multiple regression and are easily obtainable from published sources

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APPENDIX A

Table 1

Electrical Conductivity By Date
(uS/cm)

Date	#1	#2	#3	#4	#5	#6	#7	#8
April 14	88	109	64	45	60	44	30	27
April 20	73	91	58	40	51	48	30	29
April 29	81	92	66	43	63	50	31	30
May 13	121	153	79	56	69	46	35	27
May 19	96	122	76	52	63	47	33	27
May 26	107	144	86	53	80	48	36	34
June 3	133	165	87	65	72	49	39	28
June 8	163	179	108	83	80	50	48	32
June 15	200	197	124	101	92	54	60	40
June 19	215	204	157	104	99	55	57	75
June 23	219	205	98	78	99	53	54	81
June 30	151	192	108	79	91	54	40	35
July 5	118	152	89	74	59	48	38	33
July 7	144	163	99	81	67	47	46	31
July 14	188	194	105	106	92	44	52	32
July 21	178	191	119	97	91	54	51	29
July 27	162	208	98	91	107	54	48	36
August 4	172	174	74	82	90	45	41	56
August 11	141	162	87	86	91	44	45	56
August 18	101	126	90	71	67	50	45	39
August 25	138	177	101	81	80	48	44	31
August 28	143	176	118	86	90	50	47	34
Sept. 1	129	168	95	78	79	48	43	32
Sept. 8	154	187	102	87	89	51	41	29
Sept. 18	114	139	104	65	106	49	39	35
Sept. 21	91	112	71	52	70	43	30	28
Oct. 9	100	131	82	55	65	45	31	29
Oct. 16	90	110	75	52	68	45	30	27
Oct. 19	116	140	86	63	74	51	35	31
Oct. 30	110	136	89	61	76	53	34	33
Nov. 20	81	103	65	44	63	40	31	29
Nov. 30	74	90	59	40	60	40	30	27
Mean	130.9	152.8	91.2	70.4	78.1	48.2	40.3	35.7
Variance	1618.1	1286.0	438.6	372.1	216.8	16.0	71.8	167.7
S.Dev.	40.2	35.9	20.9	19.3	14.7	4.0	8.5	13.0

Table 2

pH By Date

Date	#1	#2	#3	#4	#5	#6	#7	#8
April 14	6.8	7.0	6.3	6.1	6.7	6.5	7.0	5.9
April 20	6.9	6.6	6.7	6.8	6.4	6.6	6.7	5.9
April 29	7.0	6.6	6.6	6.6	6.6	6.6	6.7	6.0
May 13	7.1	7.0	6.4	6.6	6.6	6.4	6.3	5.7
May 19	7.2	7.4	6.8	6.9	6.7	6.6	6.6	6.2
May 26	7.3	7.4	6.9	6.9	6.8	6.2	6.8	6.9
June 3	7.5	7.6	6.9	7.2	7.0	6.9	6.6	6.2
June 8	7.4	7.8	7.0	7.0	6.9	7.2	6.6	7.0
June 15	7.5	7.6	6.9	7.2	7.0	7.0	6.7	6.4
June 19	7.5	7.5	7.2	7.2	7.2	6.9	7.2	7.0
June 23	7.5	7.8	6.9	7.1	7.0	7.0	6.8	6.6
June 30	7.1	7.3	6.6	6.7	6.6	6.7	6.2	6.2
July 5	7.2	7.0	6.7	6.8	6.2	5.2	6.1	5.1
July 7	6.3	7.2	6.9	6.9	6.5	6.1	6.3	5.6
July 14	7.2	7.3	7.0	6.9	6.4	6.3	6.3	5.4
July 21	7.5	7.1	7.2	7.1	6.4	6.5	6.3	5.7
July 27	7.4	7.5	6.7	7.2	6.6	6.8	6.1	6.1
August 4	7.5	7.3	6.7	7.2	7.0	6.3	6.3	6.5
August 11	7.8	7.7	7.2	7.3	7.2	6.8	7.1	6.9
August 18	7.0	7.3	6.9	6.9	6.1	6.6	6.4	5.0
August 25	7.5	6.9	7.2	7.1	6.4	6.0	6.3	5.4
August 28	7.4	7.4	7.1	7.0	6.6	6.4	6.4	5.5
Sept. 1	6.2	6.7	6.0	6.0	5.8	5.2	5.9	5.1
Sept. 8	7.3	6.9	6.5	6.4	6.2	6.8	6.6	5.8
Sept. 18	7.1	7.3	6.6	6.0	6.4	6.8	6.4	6.1
Sept. 21	6.4	6.1	5.8	6.2	6.1	5.0	5.5	5.7
Oct. 9	6.7	5.9	5.9	6.4	5.7	5.2	6.2	5.7
Oct. 16	6.3	5.4	5.6	6.3	5.8	5.2	4.8	4.8
Oct. 19	6.5	6.6	6.3	6.4	5.9	5.6	5.7	5.5
Oct. 30	7.3	7.1	6.9	7.0	6.5	5.5	6.5	5.4
Nov. 20	7.2	7.1	6.9	6.8	6.5	5.5	6.1	5.4
Nov. 30	7.1	7.3	6.9	6.7	6.5	5.5	5.8	5.3
Mean	7.1	7.1	6.7	6.8	6.5	6.3	6.3	5.9
Variance	0.2	0.2	0.2	0.1	0.1	0.4	0.2	0.3
S.Dev.	0.4	0.5	0.4	0.4	0.4	0.6	0.5	0.6

Table 3

DOC concentration By Date
(mg/l)

Date	#1	#2	#3	#4	#5	#6	#7	#8
April 14	3.9	4.0	5.3	3.7	8.5	13.8	10.4	19.8
April 20	2.7	2.2	4.4	3.8	10.3	22.8	12.4	33.7
April 29	4.6	3.7	5.1	3.1	14.6	21.1	14.3	30.7
May 13	4.2	4.5	5.7	4.6	13.0	28.5	18.0	31.5
May 19	4.0	3.3	6.4	3.6	14.7	35.3	21.4	38.3
May 26	4.3	3.0	5.8	4.0	18.0	31.1	22.7	38.8
June 3	4.5	3.5	5.7	4.3	15.7	44.5	23.5	73.4
June 8	3.3	4.2	4.7	3.4	16.2	31.9	36.1	39.9
June 15	3.9	2.9	13.8	3.7	14.7	30.2	34.4	43.0
June 19	1.9	1.8	5.3	2.4	10.3	20.9	14.8	41.8
June 23	3.0	3.6	7.6	3.4	17.1	28.8	17.9	32.7
June 30	2.9	2.9	5.9	2.5	19.3	30.0	20.6	25.4
July 5	2.5	2.9	5.4	2.4	14.5	35.7	20.7	37.3
July 7	2.3	1.8	4.0	2.3	11.5	29.6	19.4	39.9
July 14	2.5	3.4	9.5	1.7	13.0	38.1	23.2	45.5
July 21	2.9	2.3	9.1	2.5	12.7	28.9	19.4	45.3
July 27	2.2	2.2	5.5	1.7	11.3	22.4	21.8	37.4
August 4	7.4	5.6	10.0	5.2	23.5	31.8	28.4	43.2
August 11	3.1	2.1	6.8	3.3	18.7	34.9	22.4	42.8
August 18	3.3	2.5	5.5	2.9	16.9	32.0	24.1	42.3
August 25	2.9	2.8	6.7	3.3	12.9	27.0	25.4	46.7
August 28	2.1	2.2	4.9	2.6	10.0	39.4	20.8	47.7
Sept. 1	2.6	2.3	6.5	3.3	10.0	36.8	23.8	51.9
Sept. 8	6.7	6.3	11.3	6.9	10.0	30.5	28.6	35.7
Sept. 18	5.0	4.9	9.6	6.4	15.8	34.7	34.4	44.5
Sept. 21	3.8	3.3	11.9	4.0	16.0	37.9	21.3	33.8
Oct. 9	6.8	5.3	9.5	5.5	18.3	46.3	24.8	46.3
Oct. 16	5.3	5.5	9.1	5.5	18.5	45.2	24.8	44.2
Oct. 19	5.5	5.2	8.9	5.0	12.8	32.8	21.7	30.7
Oct. 30	4.6	4.3	7.7	4.5	15.4	37.6	20.6	38.1
Nov. 20	4.5	3.8	6.7	4.7	17.1	35.6	14.8	42.9
Nov. 30	4.7	4.2	6.6	4.9	11.6	30.1	14.3	35.8
Mean	3.9	3.5	7.2	3.8	14.5	32.1	21.9	40.0
Variance	1.9	1.4	5.6	1.6	11.5	49.9	35.4	81.4
S.Dev.	1.4	1.2	2.4	1.3	3.4	7.1	6.0	9.0

APPENDIX B

Table 1. Results from a non-parametric test (NPAR1WAY) of DOC data for the original eight catchments

Table 2 Results of correlation analysis (CORR) on the data set for the original eight catchments

Table 3 Results of a test for multicollinearity (COLLIN)

Abbreviations used in this Appendix are.

LDOC = natural log of DOC Concentration.
LPCTWET = natural log of Percentage Wetland
LDRAIN = natural log of the Drainage.
LSLOPE = natural log of the Slope
LPCTFOR = natural log of the Percentage Forest
LAREA = natural log of the Area.

Table 1

Analysis For Variable DOC Classified By Variable Catchment

Analysis Of Variance

Level	N	Mean	Among MS	Within MS
Non-wetland	4	4.35	1030 58	62 17
Wetland	4	27.05		
			F Value	Prob > F
			16.58	0 00066

Wilcoxon Scores (Rank Sums)

Level	N	Sum of Scores	Expected Under Ho	Std. Dev Under Ho	Mean Score
Non-wetland	4	10.00	18 00	3 46	2 50
Wetland	4	26.00	18.00	3.46	6.50

Wilcoxon 2-sample Test (Normal Approximation)
(With Continuity Correction Of 0 5)

S = 10 00 Z = -2 1651 Prob> |Z| = 0 0304

T-test Approximation Significance = 0.0671

Kruskal-Wallis Test (Chi-Square Approximation)
Chi-Square = 5.33 DF = 1 Prob > Chi-Square = 0.0209

Note: Taken from SAS (1982) printout of PROC REG Chi-Square value is the test (underlined value) statistic for the explanation in the text.

Table 2

Results Of The CORR Procedure
A Test For Correlation Between Variables

Pearson Correlation Matrix

	LDOC	LPCTWET	LSLOPE	LDRAIN	LPCTFOR	LAREA
LDOC	1 000	0 924	-0.868	-0.943	0.688	0.700
LPCTWET	0.924	1.000	-0.670	-0.926	0.816	0.810
LSLOPE	-0.868	-0.670	1.000	0.792	-0.487	-0.453
LDRAIN	-0 943	-0 926	0.792	1.000	-0.584	-0 740
LPCTFOR	0 688	0 816	-0.487	-0.584	1 000	0.740
LAREA	0 700	0.810	-0.453	-0.740	0.740	1.000

Note All values are significant between 0.001 and 0.260 level of confidence. From PROC CORR printout (SAS, 1982)

Table 3

Diagnostic Test For Multicollinearity

Parameter Estimates

Variable	DF	Estimate	S.E.	t (HO. b=0)	p > t
Intercept	1	5.197	0.823	6 320	0 003
Lpctwet	1	0 150	0.070	2 151	0.098
Lslope	1	-0.920	0.341	-2.693	0 055
Ldrain	1	-0 245	0 618	-0 396	0.712

Collinearity Diagnostics

Number	Condition Number	Var Prop. Intercept	Var Prop Lpctwet	Var. Prop. Lslope	Var. Prop. Ldrainage
1	1 000	0 001	0.000	0 000	0.003
2	1 581	0 000	0.100	0.000	0 001
3	11.935	0 148	0.866	0.010	0 711
4	25 761	0.851	0 035	0.990	0 285

Note From PROC REG printout (SAS, 1982).

APPENDIX C

TABLE 1

Cation, DOC, and Anion Concentrations

Date	Catchment	H^+	Ca^{++}	K^+	Mg^+	Na^+	Fe	DOC	Cl^-	NO_3^-	SO_4^{--}	CO_3^{--}
20/11	1 f	0.1	394	22	183	90	5	6 7	108	24	182	374
	2	0 2	225	7	13	51	5	4.7	46	11	184	266
	3 f	0 1	527	23	228	93	5	4 5	131	23	204	590
	4 f	0 1	670	25	293	101	5	3.8	174	58	204	758
	5 *	0 8	229	9	78	54	8	14.8	58	3	126	80
	6 * f	3 0	403	11	86	122	17	35.6	142	3	167	34
	7 *	4 0	294	8	81	44	20	42 9	51	1	128	14
	8 * f	0 3	357	25	162	88	6	17 1	154	30	188	262
30/11	1 f	0 1	334	21	164	70	5	6.6	101	26	183	386
	2	0 2	201	4	110	35	5	4 9	27	13	175	214
	3 f	0 1	441	20	192	75	5	4 7	110	14	223	520
	4 f	0 1	567	23	255	83	5	4 2	147	51	205	698
	5 *	1.6	186	5	73	44	9	4.3	77	4	132	114
	6 * f	3 0	357	7	81	124	13	30.1	144	1	174	28
	7 *	5 0	261	7	73	42	17	35.8	31	0 5	129	10
	8 * f	0 3	298	26	143	76	6	11 5	133	29	184	268

Note * denotes wetland catchments.
f denotes catchments with active farming operations
All values given in μeq/l except DOC which is mg/l.
Fe is total iron (+2 and +3).

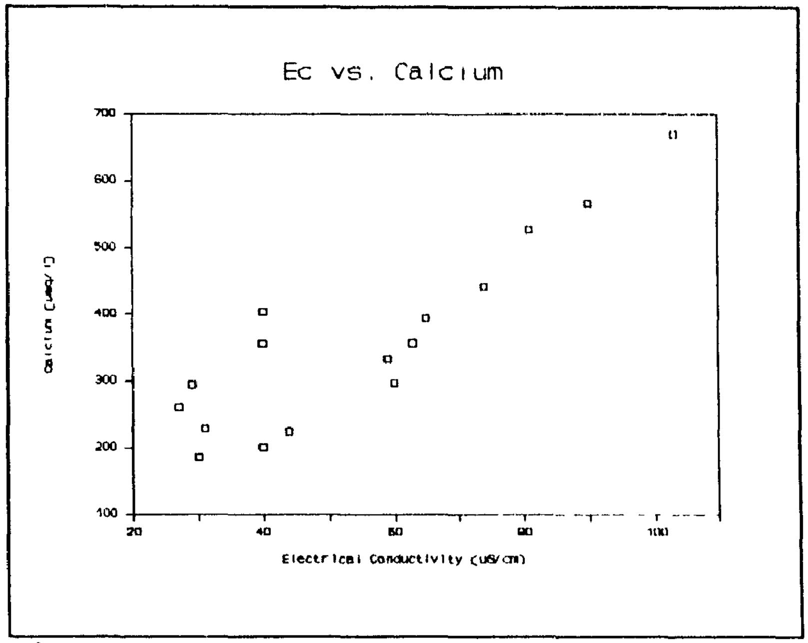

Figure 1

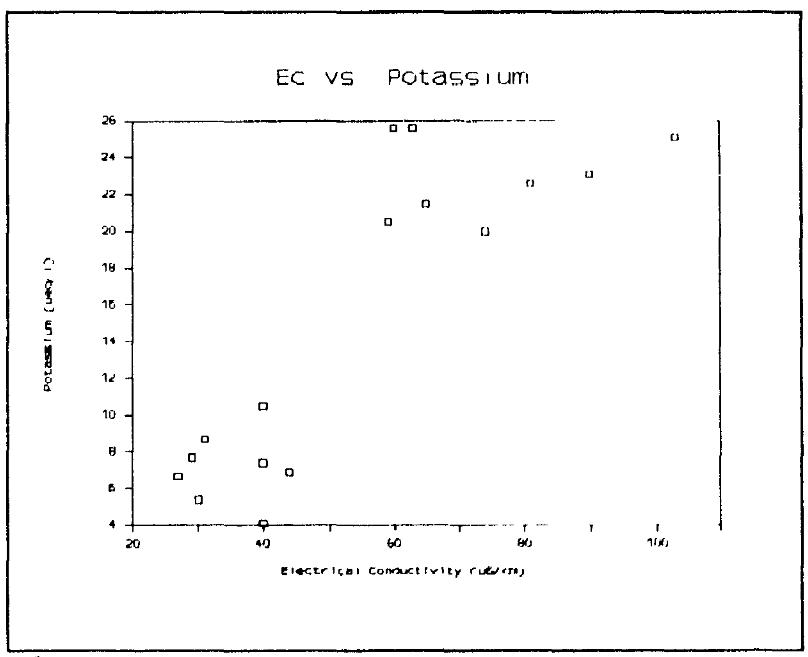

Figure 2

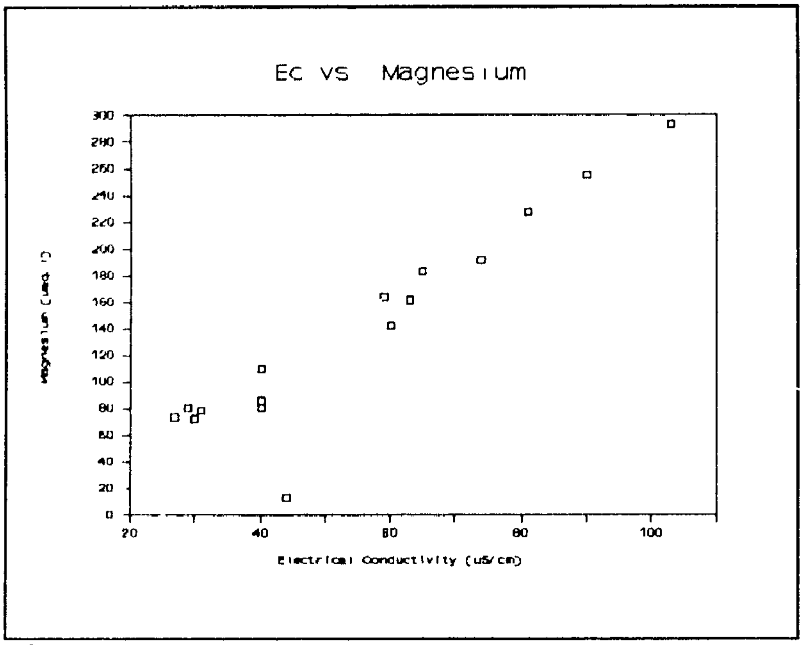

Figure 3

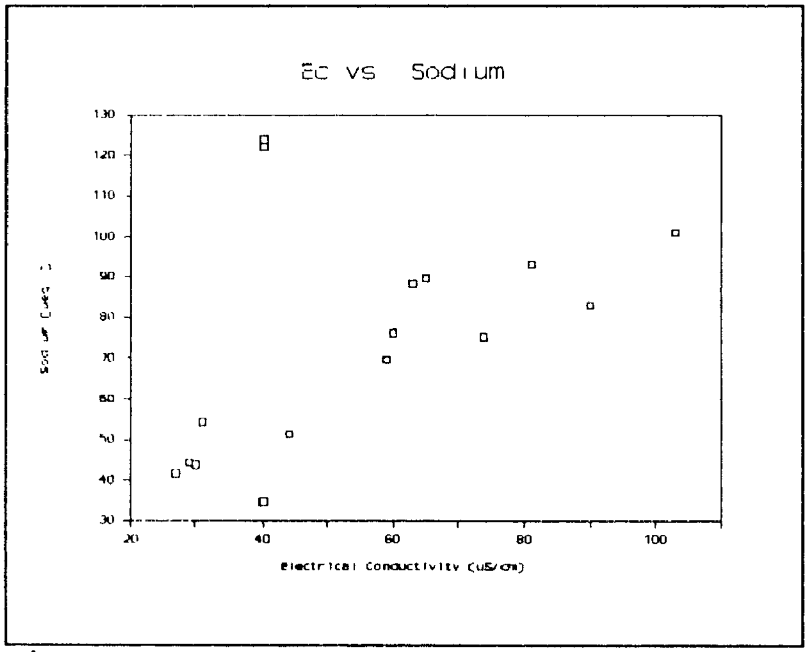

Figure 4

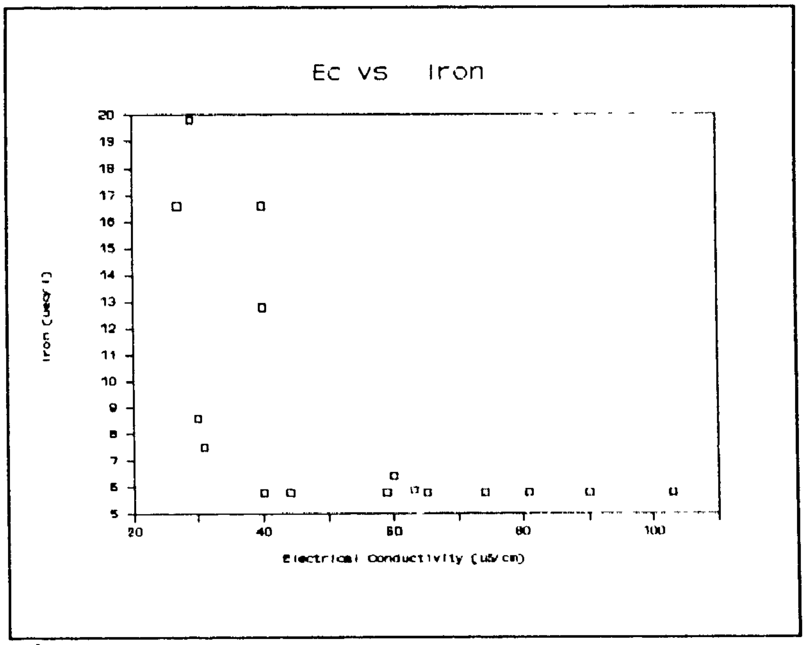

Figure 5

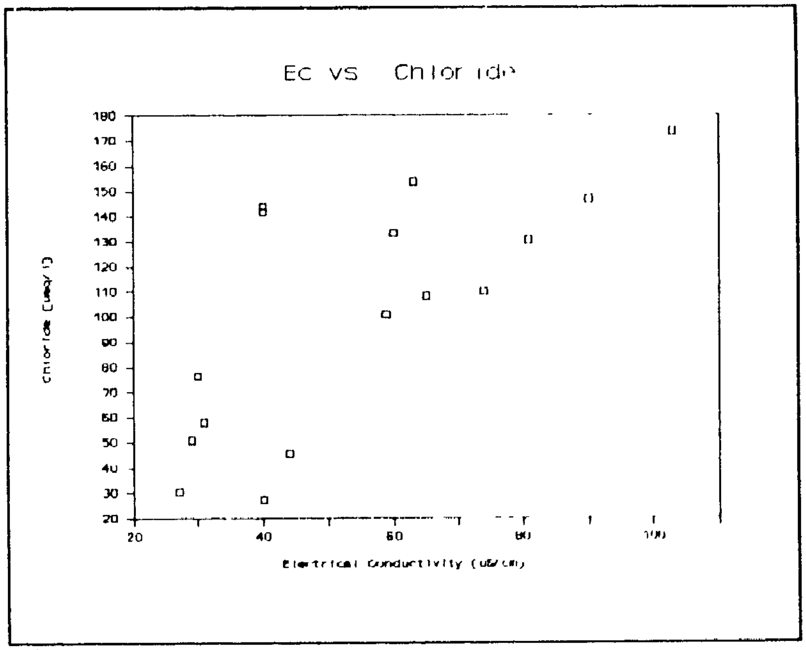

Figure 6

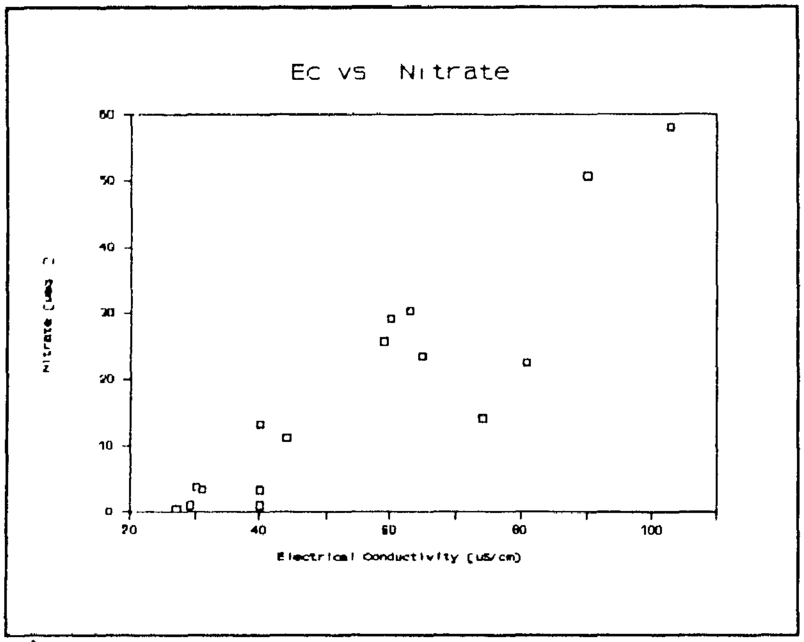

Figure 7

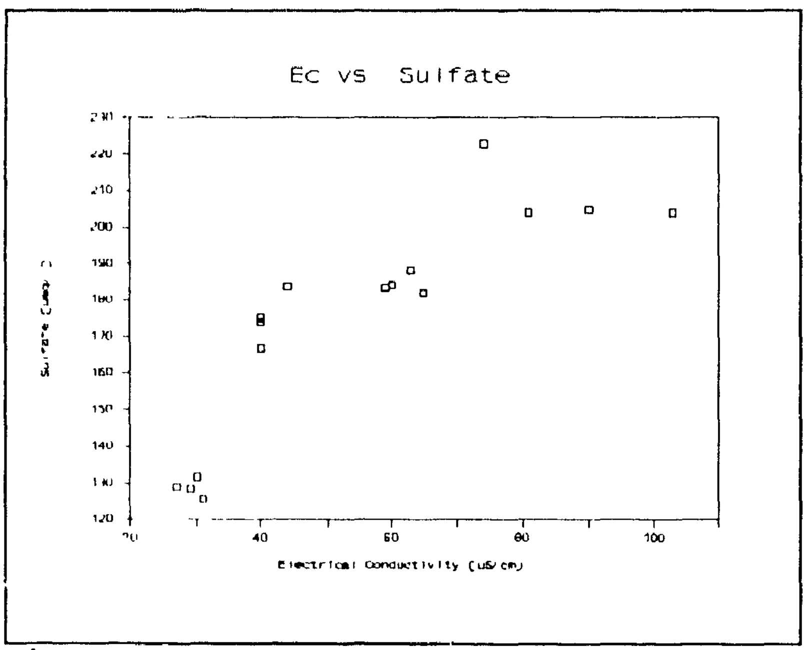

Figure 8

APPENDIX D

Table 1

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER HO:RHO=0 / N = 42

	PCTWET	SLOPE	DRAIN	PCTFOR	AREA
PCTWET	1 00000 0 0000	-0.64647 0.0001	-0 65229 0.0001	0.18954 0 2293	0.06153 0.6987
SLOPE	-0 64647 0 0001	1.00000 0.0000	0.54740 0.0002	0 10600 0.5041	0.00839 0.9580
DRAIN	-0 65229 0 0001	0.54740 0.0002	1.00000 0.0000	-0.05484 0.7301	0.03548 0.8235
PCTFOR	0.18954 0 2293	0.10600 0.5041	-0.05484 0.7301	1 00000 0.0000	0.22504 0.1519
AREA	0 06153 0 6987	0.00839 0.9580	0.03548 0.8235	0.22504 0.1519	1 00000 0 0000

Note. Taken from SAS (1985) printout, PROC CORR.

Table 2

ANALYSIS OF VARIANCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB>F
MODEL	3	15 99201053	5.33067018	34 212	0.0001
ERROR	38	5.92090853	0.15581338		
C TOTAL	41	21.91291905			

ROOT MSE	0.394732	R-SQUARE	0.7298
DEP MEAN	2.427786	ADJ R-SQ	0.7085
C.V.	16.25893		

PARAMETER ESTIMATES

VARIABLE	DF	PARAMETER ESTIMATE	STANDARD ERROR	T FOR H0 PARAMETER=0	PROB > |T|
INTERCEP	1	2 37854130	0.24114496	9.864	0 0001
PCTWET	1	0.01888660	0 004120823	4 583	0 0001
SLOPE	1	-0.01426990	0 005435837	-2 625	0 0124
DRAIN	1	-0.05242736	0 07419908	-0 707	0 4841

COLLINEARITY DIAGNOSTICS

NUMBER	EIGENVALUE	CONDITION NUMBER	VAR PROP INTERCEP	VAR PROP PCTWET	VAR PROP SLOPE	VAR PROP DRAIN
1	2 953206	1 000000	0.0070	0 0108	0 0198	0 0121
2	0.856631	1 856735	0.0013	0 1840	0 0668	0 0093
3	0.148802	4 454944	0 0095	0 0903	0 8011	0 3439
4	0.041361	8 449849	0.9822	0.7148	0 1124	0 6347

Note: Taken from SAS (1985) printout, PROC REG.